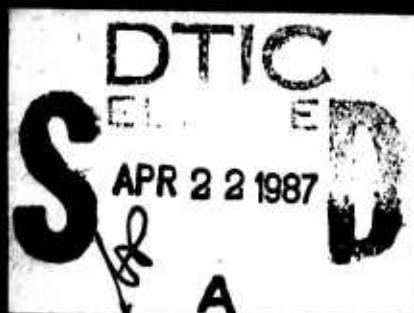


Fire Safety Aspects
of
Polymeric Materials



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VOLUME I
MATERIALS:
STATE OF
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A Report by
National Materials Advisory Board
National Academy of Sciences

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**Fire Safety Aspects
of
Polymeric Materials**

**VOLUME 1
MATERIALS:
STATE OF
THE ART**

Report of
The Committee on Fire Safety
Aspects of Polymeric Materials

**NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council**

Publication NMAB 318-1
National Academy of Sciences
Washington, D. C.
1977

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VOLUME 1 – MATERIALS: STATE OF THE ART
Fire Safety Aspects of Polymeric Materials

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NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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FOREWORD

This volume is one of a series of reports on the fire safety aspects of polymeric materials. The work reported here represents the results of the first in-depth study of this important subject. The investigation was carried out by a committee of distinguished polymer and fire technology scholars appointed by the National Academy of Sciences and operating under the aegis of the National Materials Advisory Board, a unit of the Commission on Sociotechnical Systems of the National Research Council.

Polymers are a large class of materials, most new members of which are man-made. While their versatility is demonstrated daily by their rapidly burgeoning use, there is still much that is not known or not widely understood about their properties. In particular, the burning characteristics of polymers are only now being fully appreciated and the present study is a landmark in the understanding of the fire safety of these ubiquitous materials.

In the first volumes of this series the committee has identified the limits of man's knowledge of the combustibility of the growing number of polymeric materials used commercially, the nature of the by-products of that combustion, and how fire behavior in these systems may be measured and predicted. The later volumes deal with the specific applications of polymeric materials, and in all cases the committee has put forth useful recommendations as to the direction for future actions to make the use of these materials safer for society.

Harvey Brooks, Chairman
Commission on Sociotechnical Systems

ABSTRACT

 This is the first volume in a series. The fire safety aspects of polymeric materials are examined with primary emphasis on human survival. Other volumes in the series deal with test methods, specifications and standards, special problems of smoke and toxicity, fire dynamics and scenarios, and applications to aircraft, buildings, vehicles, ships, mines and bunkers. An executive summary volume has been added to the series.

 In this volume the data is presented for polymers (natural and synthetic) in accordance with their form or conditions of use, i.e., fibers, foams, elastomers, plastics, fire retardant coatings.

VOLUMES OF THIS SERIES

- | | |
|-----------|---|
| Volume 1 | Materials: State of the Art |
| Volume 2 | Test Methods, Specifications, Standards, Glossary |
| Volume 3 | Smoke and Toxicity |
| Volume 4 | Fire Dynamics and Scenarios |
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| Volume 7 | Buildings |
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| Volume 9 | Ships |
| Volume 10 | Mines and Bunkers |

PREFACE

The National Materials Advisory Board (NMAB) of the Commission on Socio-technical Systems, National Research Council, was asked by the Department of Defense Office of Research and Engineering and the National Aeronautics and Space Administration to "initiate a broad survey of fire-suppressant polymeric materials for use in aeronautical and space vehicles, to identify needs and opportunities, assess the state of the art in fire-retardant polymers (including available materials, production, costs, data requirements, methods of test and toxicity problems), and describe a comprehensive program of research and development needed to update the technology and accelerate application where advantages will accrue in performance and economy."

In accordance with its usual practice, the NMAB convened representatives of the requesting agencies and other agencies known to be working in the field to determine how, in the national interest, the project might best be undertaken. It was quickly learned that wide duplication of interest exists. At the request of the other agencies, sponsorship was made available to all government departments and agencies with an interest in fire safety. Concurrently, the scope of the project was broadened to take account of the needs enunciated by the new sponsors as well as those of the original sponsors.

The total list of sponsors of this study now comprises Department of Agriculture, Department of Commerce (National Bureau of Standards), Department of Interior (Division of Mine Safety), Department of Housing and Urban Development, Department of Health, Education and Welfare (National Institute for Occupational Safety and Health), Department of Transportation (Federal Aviation Administration, Coast Guard), Energy Research and Development Administration, Consumer Product Safety Commission, Environmental Protection Agency, and Postal Service, as well as the original Department of Defense and National Aeronautics and Space Administration.

The Committee was originally constituted on November 30, 1972. The membership was expanded to its present status on July 26, 1973. The new scope was established after presentation of reports by liaison representatives covering needs, views of problem areas, current activities, future plans, and relevant resource materials. Tutorial presentations were made at meetings held in the Academy and during site visits, when the Committee or its panels met with experts and organizations concerned with fire safety aspects of polymeric materials. These site visits (upwards of a dozen) were an important feature of the Committee's search for authentic

information. Additional inputs on foreign fire technology were supplied by the U.S. Army Foreign Science and Technology Center and NMAB Staff.

A glossary of the terms used in the report of this Committee was compiled and will be found in Volume 2 (NMAB 318-2) of this series.

This study in its various aspects is addressed to those who formulate policy and allocate resources. A sufficient data base and bibliography has been supplied to indicate the breadth of the study.

ACKNOWLEDGEMENTS

In the drafting of this report specially valuable inputs were made by a large number of people. With apologies to those whom we have inadvertently omitted, we thank Dr. John A. Parker, Chief, Chemical Programs Office, NASA-Ames Research Center, Mr. Jack Ross, Chief, Clothing Division, U.S. Air Force, Dr. George B. Thomas, Head, Plastics Laboratory, Army Materials and Mechanics Research Center, Mr. Herbert Eichner, retired, U.S. Forest Products Laboratory, John R. Pailthorp and John J. McEvoy, E. I. duPont de Nemours and Company, Ludwig Rebenfeld and Bernard Miller, The Textile Research Institute.

The Committee panel charged with evolving the first working draft of this report included Dr. Alfred E. Brown, Dr. John M. Butler, Dr. Alfred R. Gilbert, Dr. Raymond R. Hindersinn, Dr. Eli M. Pearce, Dr. Arnold Rosenthal, Dr. Giuliana C. Tesoro, and Dr. Nicholas W. Tschoegl. The final draft was coordinated by Dr. Tschoegl.

I acknowledge with gratitude the assistance in this project of Dr. Robert S. Shane, NMAB Staff Scientist, and Miss Carolyn Tuchis, our able secretary.

Dr. Herman F. Mark
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CHAPTER 1

INTRODUCTION

1.1 Scope and Methodology of the Study

This volume is the first in a series of reports prepared by the Committee on Fire Safety Aspects of Polymeric Materials of the National Materials Advisory Board (NMAB). The charge to the Committee was set forth in presentations made by the various sponsoring agencies. Early in its deliberations, however, the Committee concluded that its original charge required some modification and expansion if the crucial issues were to be fully examined and the needs of the sponsoring organizations filled. Accordingly, it was agreed that the Committee would direct its attention to the behavior of polymeric materials in a fire situation with special emphasis on human-safety considerations. Excluded from consideration were fire fighting, therapy after fire-caused injury, and mechanical aspects of design not related to fire safety.

The work of the Committee includes (1) a survey of the state of pertinent knowledge; (2) identification of gaps in that knowledge; (3) identification of work in progress; (4) evaluation of work as it relates to the identified gaps; (5) development of conclusions; (6) formulation of recommendations for action by appropriate public and private agencies; and (7) estimation, when appropriate, of the benefits that might accrue through implementation of the recommendations. Within this framework, functional areas were addressed as they related to specific situations; end uses were considered when fire was a design consideration and when the end uses are of concern to the sponsors of the study.

Attention was given to natural and synthetic polymeric materials primarily in terms of their nature, composition, structure, relation to processing, and geometry (i.e., film, foam, fiber, etc.), but special aspects relating to their incorporation into an end-use component or structure also were included. Test methods, specifications, definitions, and standards that deal with the foregoing were considered. Regulations, however, were dealt with only in relation to end uses.

The products of combustion, including smoke and toxic substances, were considered in terms of their effects on human safety; morbidity and mortality were treated only as a function of the materials found among the products of combustion. The question of potential exposure to fire-retardant polymers, including skin contact, in situations not including pyrolysis and combustion were addressed as deemed appropriate by the Committee in relation to various end uses.

In an effort to clarify the understanding of the phenomena accompanying fire, consideration was given to the mechanics of mass and energy transfer (fire

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dynamics). The opportunity to develop one or more scenarios to guide thinking was provided; however, as noted above, fire fighting was not considered. To assist those who might use natural or synthetic polymers in components or structures, consideration also was given to design principles and criteria.

In organizing its work, the Committee concluded that its analysis of the fire safety of polymeric materials should consider the materials themselves, the fire dynamics situation, and the large societal systems affected. This decision led to the development of a reporting structure that provides for separate treatment of the technical and functional aspects of the problem and the aspects of product end use.

Accordingly, as the Committee completes segments of its work, its findings will be presented in the following five disciplinary and five end-use reports:

- Volume 1 Materials: State of the Art
- Volume 2 Test Methods, Specifications, Standards and Glossary
- Volume 3 Special Problems of Smoke and Toxicity
- Volume 4 Fire Dynamics and Scenarios
- Volume 5 Executive Summary
- Volume 6 Aircraft – (Civil and Military)
- Volume 7 Residential, Non-residential, and Custodial Buildings
- Volume 8 Vehicles – (Railed and Unrailed)
- Volume 9 Ships
- Volume 10 Mines and Bunkers

Some of the polymer applications and characteristics are in the classified literature, and the members of the Committee with security clearance believed that this information could best be handled by special meetings and addendum reports to be prepared after the basic report volumes were completed. Thus, the bulk of the output of the Committee would be freely available to the public. Considering the breadth of the fire safety problem, it is believed that exclusion of classified information at this time will not materially affect the Committee's conclusions.

1.2 Scope and Limitations of this Report

This volume describes the state of the art of materials and is intended only to provide a point of departure from which a more detailed assessment of the fire safety aspects of polymeric materials can be undertaken. In combination with the references cited, it should establish the background for the beginning of sound understandings of the fire safety problems associated with polymeric materials, of the direction that further developments should take, and, in some instances, of the basis for proper choice of materials to meet requirements of a given application.

Volume 1, Materials: State of the Art, consists of eight chapters and References as follows:

INTRODUCTION

1. Introduction
2. Conclusions and Recommendations
3. Wood and Wood Products
4. Fibers
5. Elastomers
6. Plastics
7. Foams
8. Fire Retardant Coatings

References

Chapters 3 through 8 provide general information on the fire safety aspects of the main classes of natural and synthetic polymers categorized by end uses. Because these chapters were prepared so as to be reasonably complete in themselves, some unavoidable redundancy appears in reading from chapter to chapter. Proprietary compositions such as polymer-based household preparations, industrial aids, and cosmetics are not covered in detail, although, if their principal constituents are known, some information may be found in the appropriate chapters of this volume. Fuels, lubricants, hydraulic fluids, and similar low-molecular-weight compounds do not fall within the scope of this Committee's study.

1.3 General Considerations of the Fire Safety Aspects of Polymeric Materials

The Committee wishes to emphasize that statements about the fire safety aspects of polymeric materials, including those that are judgmental or concern the fire safety of materials in particular end uses, apply only to the specific situation they describe. The fire safety suitability of a material for a particular application depends on many factors, e.g., ease of access, ease of egress, proximity of the ignition hazard, proximity of other materials, duration of the fire, the thermal flux generated, the source of ignition, the ambient oxygen partial pressure, as well as the fire and smoke detection and suppression systems in place. Therefore, statements in this volume must not be taken out of context and applied to the use of identical materials in other situations.

Development of polymeric materials with improved fire safety characteristics is a process in which competing requirements must be reconciled, because the improvement must be achieved at acceptable cost without impairment of those physical properties for which the polymer is selected, and with attention to the proper balance of the fire safety characteristics (e.g., in some situations an improvement in ease of ignition or flame spread at the cost of increasing the production of smoke or toxic combustion products would not be tolerable).

Furthermore, materials selection is only one way to reduce the ever-present threat of fire. General fire-consciousness, structural design, use environment, fire detection, and fire fighting are equally important aspects of coping with fire hazards.

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Few quantitative measurements of the fire safety characteristics of polymeric materials are quoted in this volume. This is intentional and aims to avoid improper interpretation or extrapolation of numbers beyond the limits of their usefulness. Quantitative information, if available, may be found in the references listed throughout the volume.

Polymers are generally treated under their most widely used chemical names. Tradenames have been used only where they seemed appropriate. An extensive list of tradenames has been published by Titus (1974). More restricted, but useful, lists may be found in the Appendices of *Textbook on Polymer Science* by Dr. Fred W. Billmeyer, Jr., Interscience Publishers, March 1966, and in the *Modern Plastics Encyclopedia* (MPE), 1974.

1.4 Approaches to Improving the Fire Safety Characteristics of Polymeric Materials

No organic polymeric material can withstand intense and prolonged heat without degradation, even in the absence of oxygen. Given sufficient oxygen and energy input, all commercial polymeric materials will burn. The terms fire safe, fire proof, fire resistant, fire retarded, flame resistant, flame retardant, etc., express degrees of resistance of a material to burning, but most terms in current use lack precise meaning. The Committee has attempted to collect and define terms relating to fire science and technology in the Glossary appended to Volume 2, Test Methods, Specifications, and Standards, and also in Volume 6, Aircraft - (Civil and Military).

For purposes of this volume, fire safety means primarily immunity of humans from damage caused by a fire; a fire retardant is a substance or treatment that reduces the flammability of a material; and a fire retarded polymer is one whose flammability has been decreased by the incorporation of a fire retardant. The terms "fire retardant" and "flame retardant" are used interchangeably in this volume.

Essentially two avenues are open to the preparation of polymers with improved fire performance. The first consists of the development of new polymers whose fire safety characteristics are inherent in their structure. Although some materials in this class are available commercially now, this approach is still largely experimental. It will be discussed subsequently, particularly in Section 4.5 (new fibers), and Sections 6.5 and 6.6 (new plastics). In the field of elastomers and the related field of elastomeric foams (see Chapters 5 and 7 respectively), novel approaches are still lacking. With some promising exceptions (e.g., some chlorine-containing rubbers, fluoroelastomers, silicone rubbers, and phosphonitrilic elastomers), polymeric molecules with inherently improved fire performance are rigid molecules that lack the room-temperature flexibility required of elastomers.

The second approach consists of improving the fire safety characteristics of available lower cost materials by adding fire retardants. At present this approach is

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technologically and commercially the more important of the two avenues. It may take the form of the application of a coating to the surface of the material or the incorporation of a fire retardant into its bulk at some appropriate stage of processing.

Use of coatings to protect flammable substances is one of the oldest methods of fire retardation. In this approach, a fire retardant coating is either applied to the surface of the material (non-intumescence coating) or produced in the presence of the flame —intumescence coating). Such fire retardant coatings are discussed further in Chapter 8.

Polymers may be fire retarded by partial replacement of a conventional monomer in a polymer chain with a special fire-retardant monomer and/or by introducing into the bulk of the material certain fillers, e.g., hydrated alumina, or by introducing certain compounds with fire-retardant properties. The first two methods lower the fire load by heat absorption or by providing an inert diluent for the fuel. Fire retardants are usually halogen, phosphorus, nitrogen, antimony, or boron compounds; they can be used in combination.

Fire retardation by addition of retardants (copolymerized or physically blended) is discussed in more details in Sections 3.3 (wood), 4.2.1 (natural fibers), 4.3.1 (synthetic fibers), 4.7 (fibers in general), 5.2 (elastomers), and 6.2 (plastics). These sections also discuss briefly some theories that have been advanced for explaining the action of fire retardants. For more comprehensive reviews of the subject, the reader is referred to the work of Hindersinn and Wagner (1967), Lyons (1970), the volumes edited by Kuryla and Papa (1973), and that by Lewin, Atlas, and Pearce (1975).

1.5 Economic Aspects

According to the Report of the National Commission on Fire Prevention and Control (1973), fire claims nearly 12,000 lives in the United States. The report estimates the annual cost of fire in the United States at 11.4 billion dollars.

Cost is an important aspect of fire retardation. Many thermally stable polymers with superior fire safety characteristics are currently expensive, in fact, too expensive for routine use in all but special applications in which the high performance requirements justify the cost. Advances in production technology and increases in consumption may be expected to lower costs, and, in some cases, to allow some of these polymers to be more widely used.

Application of fire retardant coatings can be a cost-effective approach. However, it is limited to a relatively small number of uses.

The cost of fire retardation by the incorporation of a fire retardant in the polymer varies greatly, according to the performance level desired, the particular compound or treatment used, and the offset in fabrication costs. When it can be incorporated as a part of the production of the polymer, it can be more economical

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than when it is used as an after-treatment. Thus, the impregnation of wood with fire retardants generally increases the cost of lumber by 50 to 100 percent, while substantially lower costs can be achieved in fire retardation of synthetic polymers, at least in some instances. Fire retardation generally increases the cost of the material, except when the desired measure of protection can be obtained with inexpensive inert fillers without undue detriment to polymer properties.

1.6 Environmental Aspects

Some halogenated organic compounds, organophosphorous compounds, metal salts, and other inorganic substances, like antimony oxide and ferrocene, may accumulate in the environment, concentrate in food chains, and produce a variety of health and ecological effects. Skin contact, contamination of foods, and inhalation can occur whether combustion is involved or not. These possibilities are superimposed on special types of exposure which arise during the manufacture, application, and disposal of the materials. In the absence of a general understanding, each of these potential hazards must be considered as a special case in the fire retardation of polymers and evaluated in the context of new technology or new products proposed for commercial use.

1.7 Educational Aspects

During its deliberations the Committee was often presented with clear indications that many unnecessary fire hazards result from a general lack of knowledge and appreciation of fire safety problems in the use of polymeric materials. This lack of knowledge by the general public is understandable, if no less tragic in its consequences. Many uses of synthetic polymers are relatively new and no "conventional wisdom" has yet developed concerning their fire performance. Many synthetic polymer materials burn differently from the more familiar natural ones. They may melt and drip and often give off dense and acrid smoke. Although some are less flammable than conventional materials like wood or cotton, others burn with more intense flame and resist convention efforts of fire fighting. Such features tend to promote panic and can lead to damage and loss of life, which might have been avoided with a better understanding of the performance of materials in a fire. Better understanding of the fire hazards presented by polymeric materials must be promoted through educational efforts (National Commission on Fire Prevention and Control, 1973; Tabor, 1975).

It is more difficult to justify the lack of understanding of polymer properties in general and their fire safety aspects in particular among practicing engineers, architects, designers, and builders. Quite generally, professionals who routinely recommend and specify the use of polymers are without even rudimentary training in polymeric materials. Undoubtedly, the general lack of understanding of the nature and properties of polymers results from the fact that polymer science and engineer-

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ing are only 30-40 years old, and acceptance of the need for training in these relatively new materials in schools has been generally slow at both the secondary and tertiary levels. Salamone, Deanin, Young, and Pearce (1973) among others have briefly discussed the reasons. They have also tabulated information on polymer science and engineering education in the United States. The Committee wishes to add its voice to those who are beginning to cry out for increased attention to polymeric materials in science and engineering curricula.

1.8 Planning and Coordination of Research Efforts

In the course of its activities, the Committee listened to presentations by the sponsors and other qualified groups describing their problems and programs in the area of fire safety aspects of polymeric materials. On the basis of this input, it became apparent to the Committee that planning, coordination, and dissemination of these efforts could be improved. The Committee is aware of the establishment of the National Fire Prevention and Control Administration under the appropriate act of 1974 and recognizes that the frame of reference under which this Administration will work is currently being clarified. The Committee is also aware of major ongoing programs at the National Bureau of Standards Center for Fire Research and in various committees of the American Society for Testing and Materials.

The Committee recognized that extensive research aimed at the development of products with improved fire performance is being conducted in industrial organizations. Information on much of this ongoing research is considered proprietary and is not discussed in this report.

The Committee senses a general need for better communication and wider dissemination of results in the fire research community, comprising government agencies as well as university and industrial research laboratories. A number of conferences are now being held on fire problems. Specialized journals are appearing and abstracting services and data banks are being developed, but there is some concern with the fact that there is still no general access to potentially important technical information. The Committee recognizes that the National Fire Prevention and Control Administration is planning the establishment of a National Fire Data Center (Tabor, 1975). It is hoped that its existence will improve the dissemination of research results.

CHAPTER 2

CONCLUSIONS AND RECOMMENDATIONS

2.1 Introduction

This chapter summarizes the conclusions and recommendations reached by the Committee after having reviewed the state of the art of polymeric materials with respect to fire safety. These conclusions and recommendations are not intended to reflect any order of importance or priority. Moreover, the Committee did not feel that it should provide quantitative statements of effort associated with each recommendation.

These conclusions and recommendations have been subdivided into three sections. The first section presents summary conclusions upon which no specific recommendations are based. The second section lists general conclusions and recommendations based on them. Finally, specific conclusions and recommendations concerned with particular materials areas are presented in the third section.

2.2 Summary Conclusions

Given sufficient oxygen and heat input, all organic polymers will burn.

Absolute fire safety of polymeric materials does not exist. There are always trade-offs in safety, utility, and costs.

Billions of pounds of synthetic and natural polymers are used annually in the United States without presenting unmanageable fire safety problems. However, some uses of polymeric materials have seriously augmented the fire hazard. With increased volume and diversity of uses, such hazards could increase further.

Many synthetic organic polymers burn in a manner differing from that of the more familiar natural polymers such as wood, paper, cotton, or wool. Some synthetics burn much faster, some give off much more smoke, some evolve potentially noxious and toxic gases, and some melt and drip. Others burn less readily than the natural polymers.

As the diversity and amount of polymeric materials used in confined areas (dwellings, vehicles, etc.) increases, the problems presented by the generation of smoke and toxic gases in a fire also increase. Objective information fully defining the extent and nature of this hazard is not available.

The fire safety of many polymers has been improved by the incorporation of fillers and/or compounds containing halogens, phosphorus, and/or antimony. In general, this is effective in resisting small ignition sources or low thermal fluxes in large-scale fires. Most of these systems burn readily and may lead to increased smoke generation or increased production of toxic and/or corrosive combustion products.

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2.3 General Conclusions and Recommendations

Conclusions: Assessment of the fire safety characteristics of polymeric materials is hampered by a lack of adequate test methods and performance criteria. Many current developmental efforts simply seek to improve the fire performance of well known materials so that they comply with existing and often inadequate standards (also see Volume 2 of this series of reports). *Recommendations:* Define and implement a broadly based program to develop meaningful test methods and standards that will more accurately define the flammability characteristics of polymeric materials in the broad spectrum of fire situations. Develop tests and protocols for ascertaining the safety hazards of combustion products of polymeric materials and materials combinations.

Conclusion: The fire safety characteristics of polymeric materials must be viewed in a systems context. Fire safe design, fire detection, fire fighting, the end use, environmental effects and general fire consciousness are at least equally important aspects of the total picture. Methods for fire safety analysis are ill-defined and/or seldom used (also see Volume 4 of this series of reports). *Recommendation:* Develop fire safety systems analysis methods to guide materials selection so that the overall fire safety assessment can be based on the material, design, environment, detection, and fire fighting factors.

Conclusion: The planning, coordination, and dissemination of research efforts by government agencies need improvement, and there is no central data bank on fire safety with unrestricted access to the fire research community. *Recommendation:* Create an overall program that will coordinate the government-supported work on fire safety of polymeric materials and disseminate its results.

Conclusion: Designers, architects, and engineers generally lack training regarding the properties of polymeric materials they use and specify. They are usually uninformed about the fire safety problems associated with these materials. *Recommendations:* Require greatly increased emphasis on fire safety of polymeric materials in curricula for designers, architects, and engineers; continue efforts to eliminate misrepresentation of fire safety in promotional materials and advertisements.

Conclusion: The general public lacks understanding of the fire safety aspects of polymeric materials. Because of the mode of burning, some synthetics may differ from the more familiar natural polymers. Those synthetics often present unexpected fire situations with which the average person cannot cope. *Recommendation:* Develop a sound educational program for all age levels to better acquaint the public with the fire safety aspects of polymeric materials, their products, and their uses.

Conclusion: Apprehension exists that the fire retardation of polymers in nonfire and/or fire situations may have an adverse impact on the environment. *Recommendation:* In all programs, maintain an awareness of the potential threat to the environment of additives, monomers, degradation products, and other materials used in the synthetics and modification of polymers for improved fire safety characteristics.

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Conclusion: There is a serious lack of knowledge concerning the relationships of chemical and physical composition of polymeric products to the emission of smoke and toxic gas formation during combustion. *Recommendation:* Initiate programs to determine the relationship of chemical and physical components of polymeric products to the evolution of smoke and toxic gas formation.

Conclusion: There is a lack of basic knowledge concerning the relationship between the chemical and physical properties of polymers and fire dynamics parameters (flame spread, ease of ignition, etc.) as well as the way these relationships are affected by aging (see Volume 4 of this series of reports). *Recommendation:* Initiate programs to further increase basic knowledge of the relationships between the chemical and physical properties of polymers and fire dynamics parameters and the way these relationships are affected by aging.

Conclusion: Polymeric materials with improved fire safety characteristics that are available today have one or more deficiencies such as high cost, fabrication difficulties, and toxic and corrosive combustion products. By using polymers with appropriate molecular structures, it has been shown that one can produce polymers with fire safety characteristics that meet most end-use requirements. To gain large-scale acceptance, these materials must become available at reasonable cost. *Recommendation:* Support approaches to improving the fire safety of the high-volume, low-cost polymers (see Table 7). Establish incentives to accelerate the introduction and commercialization of new materials with improved fire safety characteristics. Increase the development effort on char-forming systems with particular emphasis on lowering the fabrication cost.

2.4 Specific Conclusions and Recommendations

Conclusion: Because of its low cost, comfort, and versatility, elastomeric polyurethane cushioning is widely used. However, such cushioning can burn readily, even when fire-retarded. New materials and/or new approaches using current materials are urgently needed. *Recommendation:* Institute and support research and development programs aimed at improving the fire safety characteristics of cushioning systems. Such programs should consider cost effectiveness *inter alia*.

Conclusion: Mass-market textile fibers (see Table 3) do not offer protection against direct exposure to flames. The fire safety aspects of fiber blends cannot be predicted from a knowledge of the behavior of individual components (e.g., effective and economical fire-retardant treatments for popular blends of cotton and polyester fibers are still the subject of considerable research). Carpet systems vary greatly in their response to fire. Systems that are safe for uses in critical areas such as aircraft and nursing homes need to be defined and/or developed. *Recommendation:* Institute and support a program to define the overall fire safety problems (flammability, smoke and toxic gases, etc.) of fiber-based materials and to develop improved materials as appropriate.

Conclusion: Concern exists about potential fire hazards associated with the

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rapidly increasing use of polymeric structural and insulating foams, particularly in the areas of kitchen cabinets, furniture applications, and decorative paneling. *Recommendations:* Define and implement a broadly based program to develop meaningful test methods and standards that will more accurately establish the flammability characteristics of these polymeric systems in the broad spectrum of fire situations. Develop fire safety systems analysis methods to guide the materials selection process so that the overall fire safety assessment of these foams considers composition, end use, material design, environment, detection, and fire fighting factors.

Conclusion: The use of intumescent coatings can be a cost-effective way to enhance the fire safety of some polymeric products. *Recommendation:* Expand the materials and applications studies on intumescent coatings with emphasis on lowering the cost and improving coating performance and aesthetics.

CHAPTER 3

WOOD AND WOOD PRODUCTS

3.1 Introduction

The appearance, texture, weight, cost, insulation characteristics, ease of fabrication and availability of wood and wood-base products have long contributed to their wide use in housing and building construction in the United States. While the combustibility of untreated wood has limited its application in some types of building, the use of proper fire safety design (for such items as heating systems, electrical systems, and exits), the combination of wood with fire retardant materials, and the slow charring rate and good strength retention of large wooden members in fire situations, have lead to the general acceptance of untreated wood as a relatively safe building material.

Considerable technical information is available on methods for treating wood to reduce its flammability as well as initial rate of heat release and to render it self-extinguishing of flame and glow. These treatments have not been applied widely because improvement in fire safety has not been sufficient to warrant the additional cost. Moreover such treatments can adversely affect some non-fire-related properties of wood.

3.2 Composition and Properties

The cellular structure of wood is complex. Cells are bound together by cementing layers. The cell walls are composed of cellulose, from 18 to 25 percent (dry wood weight) lignin, and, depending upon species and growth conditions, from 4 to 20 percent (dry wood weight) of other materials including aliphatic and aromatic hydrocarbons, alcohols, acids, aldehydes, esters, ethers, tannins, fixed oils, resin acids, proteins and alkaloids.

The elementary composition of most wood species used for construction is approximately 49 ± 1 percent carbon, 6.1 ± 0.1 percent hydrogen, 0.1 to 0.3 percent nitrogen and 0.2 to 1.0 percent ash; the remainder is oxygen (Wise and Jann, 1944).

3.3 Fire Retardant Treatments

Treating wood with fire retardants was originated in the first century B.C. by the Romans, who used solutions of alum and vinegar. In Europe, fire retardant treatments for the wood used in ships and theaters were the subject of considerable experimentation between 1625 and 1800. In 1820, Gay-Lussac initiated the first systematic investigation of the use of salts as fire retardant treatments for fabrics

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TABLE I
SOME PROPERTIES OF WOOD

<u>PROPERTY</u>	<u>MEASURE</u>
Specific Gravity (most commercial species in the United States)	0.3 to 0.7 g/cm ³
Thermal Conductivity	
Perpendicular-to-grain (S = specific gravity; M = percent moisture)	$[S(4.78 + 0.097M) + 0.567] \times 10^{-4}$ cal/sec/cm ² /°C/cm
Parallel-to-grain	Approximately 2.5 times the thermal conductivity perpendicular to grain
Specific Heat	0.34 cal/cm ³
Thermal Diffusivity	$13 \text{ to } 19 \times 10^{-4} \text{ cm}^2/\text{sec}$
Total Heat Value	4,600 to 4,800 cal/g
Charring Rate (ASTM E119 exposure, average species)	0.065 cm/min, decreasing with increasing specific gravity and moisture content
Rapid Surface Charring	280°C
Rapid Ignition Temperatures*	
Pilot Flame	225°C (10 min) to 300°C (1 to 2 min.)
Spontaneous	360°C to 540°C
Flame Spread Classification (ASTM E84)	60 to 80 for redwood, hemlock, northern spruce, Douglas fir; up to 230 for certain pines
Smoke Developed Classification (ASTM E84)	100 to 300
Smoke Density (various species) (Thickness: 0.50 in.; maximum specific optical density)	50 to 150 flaming; 250 to 550 non-flaming
Limiting Oxygen Index	20.5 to 22.7

*The ignition temperature of wood depends on specimen size, heating conditions, time, and test method. Welker (1970) discusses some of the parameters involved in the measurement of the ignition temperature of wood.

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and other organic materials. By 1870, many of the inorganic fire retardant chemicals used today had been identified. In the early 1890's, the first U.S. patents on fire retardant treatments for wood were granted and the first commercial treatment began in New York City. Since then, the use of these treatments has fluctuated considerably. A peak was reached in 1943 when more than 5 million cubic feet of lumber and plywood were treated. Much of this treated wood was used in building hangars for dirigibles. In 1957, only 362,000 cubic feet were treated annually with retardants. Increasing recognition by authorities of the benefits of treatment caused more than a tenfold increase over the next ten years; in 1967 almost 5 million cubic feet of lumber and plywood were treated. This level of treated wood production remained approximately the same for the next four years, but increased to almost 6 million cubic feet in 1975. To put this latter figure in perspective, it must be noted that this amount represents less than 0.1 percent of the wood and plywood products produced annually in the United States.

As noted above, the cost of treating wood with fire retardants has been a principal reason for its limited use. Although the chemicals generally are inexpensive, the cost of the treatment process increases the selling price of wood and wood products by 50 to 100 percent. Further, untreated wood framing used in housing generally performs adequately in fire situations and is seldom a primary source of serious home fires. Interior wood finish materials for one and two-family housing also are seldom treated since egress from such structures is relatively easy. A much greater hazard is posed by combustible contents brought into such dwellings by the occupants. Fire retardant wood is used, however, in large buildings with assembly, educational, mercantile, and institutional occupancies, particularly in the corridors and the assembly areas.

3.3.1 Types of Fire Retardants

Fire retardants for wood are of two general types: (1) those that are impregnated into the wood or incorporated into wood products in the form of aqueous solutions, and (2) those that are applied as paints or surface coatings. Impregnation is most common, particularly for new materials, and the use of coatings has been limited primarily to materials in existing construction. Code authorities generally recognize and accept the impregnated products by the inspection label on the product, but they are reluctant to accept coating treatments that are applied on site without inspection (Eichner, 1966). Thus, the following discussion emphasizes the impregnation methods covered in Chapter 7.

3.3.2 Treatment Processes

Fire retardants are incorporated into wood under pressure. The treatment involves exposing wood to a vacuum in an autoclave, introducing a 12 to 18 percent aqueous solution of the retardants and subsequently applying air pressure. Following impregnation, the treated wood must be dried under carefully controlled

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conditions to prevent degradation, darkening, staining and grain raising. Simple surface treatment usually does not result in the required retention.

General practice in the fire retardant treatment of lumber and plywood is described in the American Wood Preservers Association (AWPA) Standards C20-70 (1970) and C27-70 (1970). The sapwoods of the more easily treated wood species usually are impregnated completely. For species with heartwood (the hard central part of the trunk of the tree), incising may be needed before treating. Lumber up to two inches thick should retain an average of at least 3 pounds of dry fire retarding chemicals per cubic foot. Thicker lumber should be penetrated to a depth of at least 1/2 inch. Only exterior grades of plywood are treated and the treating periods are shorter than for lumber. Frequently an untreated facing veneer will be bonded to the treated core of decorative hardwood plywoods.

3.3.3 Chemicals and Formulations

As noted above, most of the chemicals used in fire retardant formulations have long been known. These chemicals include ammonium phosphate, ammonium sulfate, zinc chloride, borax and boric acid. A typical fire retardant formula consists of 35 parts of zinc chloride, 35 parts of ammonium sulfate, 25 parts of boric acid and 5 parts of sodium dichromate. More recently, dicyandiamide-phosphoric acid and organic phosphorous-halogen compounds have been used in leach-resistant formulations (Lyons, 1970). These formulations have been based on both basic and empirical investigations aimed at optimizing overall performance. Zinc chloride is excellent as a flame retardant, but it tends to promote smoke development under certain conditions and is not effective as a glow inhibitor. Ammonium sulfate is the least expensive of the flame retardants and does not produce excessive smoke. Boric acid is especially effective in preventing afterglow. Sodium dichromate is added primarily to inhibit corrosive effects, but excessive amounts can promote glow.

In the formulation of fire retardant treatments, consideration also must be given to their effect on the strength, durability, hygroscopicity and corrosion properties of wood, as well as to fabrication characteristics (ease of painting, gluing and machinability) of the treated wood. Reduced performance in some applications has limited the use of fire retardant treated wood-based products; however, such problems can be minimized through use of appropriate chemical formulations and other techniques.

3.3.4 Fire Performance of Wood

Proper treatment of wood and wood-based products with fire retardant formulations decreases the rate of surface flame spread and renders them self-extinguishing of flame and glow when the external source of fire or heat is removed.

Fire retardant treatments do not, however, prevent the wood from degrading when exposed to heat. Wood treated with many chemical formulations will char at

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lower temperatures than will the untreated products, but the rate of char penetration is not greatly changed by treatment and is, at best, reduced by 20 percent (Schaffer, 1974).

The amount of smoke produced when treated wood burns depends greatly on the chemicals used in the fire retardant formulation and the fire exposure conditions. When an external flame source is present and only one end of a piece of the material is exposed to the flame, relatively little smoke is generated. If most or all of a piece is exposed to a nonflaming radiant source, more smoke may be generated from wood products treated with certain fire retardant formulations than from untreated products (Eichner and Schaffer, 1967).

Information on the effects of chemical treatments on the toxicity of the pyrolysis and combustion products of wood is very limited. Under optimum burning conditions, untreated wood produces carbon dioxide and water; but, in most fires carbon monoxide, irritant gases as well as vapors (e.g., acetic acid, formaldehyde, acrolein, glucosans, and phenols, and possibly hydrogen cyanide) are produced. The use of fire retardants reduces the percentage of tars and vapors and increases the percentage of wood retained as a charcoal residue. Inorganic fire retardant chemicals usually do not release volatile decomposition products, however, some formulations can release small amounts of ammonia or hydrochloric acid under certain conditions.

3.3.5 Theory of Fire Retardance in Wood

There are a number of theories about how fire retardant chemicals act to reduce the flammability of wood (Browne, 1958; Shafizadeh, 1968). These theories may be summarized as follows:

1. Fire retardant chemicals form a liquid or glassy layer that prevents escape of flammable products and restricts the access of air to the combustion zone.
2. The chemicals form coatings, glazes, or foams that insulate the wood surface and prevent pyrolysis.
3. The treatments increase thermal conductivity of the wood thus permitting heat to dissipate from the surface at a rate faster than it is supplied by the ignition source.
4. Fire retardant chemicals undergo chemical and physical changes that absorb enough heat to prevent wood surfaces from reaching ignition conditions.
5. Nonflammable gases released by decomposition of the fire retardant chemicals dilute the combustion gases formed by pyrolysis of the wood and form a nonflammable gaseous mixture.
6. Fire retardant chemicals release certain free radicals capable of breaking the normal combustion chain, thus restricting the flammability range for combustible gas-air mixtures.
7. Fire retardant chemicals lower the temperature at which pyrolysis starts,

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thus promoting greater char yields and reducing the formation of intermediate combustion products such as flammable tars and gases.

Recent research (Tang, 1967; Brenden, 1968; Tang and Eichner, 1968; and Beall and Eichner, 1970) involving thermogravimetric analysis, differential thermal analysis and product analysis has tended to support the latter theory (No. 7).

3.4 Fire Retardant Treatments of Other Wood Products

In addition to lumber and plywood, many other wood products are fabricated from wood chips or fibers. Of these products, panel board and paper are the most important.

Fire retardant treatments for paper and wood-based panelboard may employ the same chemicals used in treating wood and plywood. The chemicals are often added during the fabrication process. Because many effective fire retardants are water soluble, it is difficult to retain enough chemicals in the mat produced through wet forming (although some fabricators have developed "closed wet forming" systems to partially solve this problem). When it is not possible to add the chemicals during the wet-forming process, they must be applied to the mats after forming. In dry-forming processes of boards, the chemicals in either spray solution or fine powder form can be added to the fibers or chips before forming, but care must be taken to prevent the chemicals from migrating to the lower side of the mat.

Fire retardant chemicals added during fabrication must be properly selected to ensure that they do not interfere with resin bonding or board formation. Lack of consideration of this point may result in reduced strength and dimensional stability or contribute to such degradation during final hot press forming operations.

CHAPTER 4

FIBERS

4.1 Introduction

Because fibers form the main components of clothing and furnishings, their flammability characteristics are of major concern. Most polymers used as fibers are also employed as plastics or elastomers. While this chapter emphasizes the fiber aspects, references are made to the appropriate sections in other chapters of this volume for more detailed information on the chemistry, technology and fire safety aspects of given fiber forming polymers.

Fibers are discussed here under the heading of natural fibers, synthetic fibers, glass fibers, and fibers from relatively thermally stable polymers. This discussion is followed by consideration of special fire hazards posed by fiber blends, and by a brief review of fire retardant compounds and additives used in the fire retardation of fibers and textiles.

In textiles, as in many other applications of polymers, fire retardance is generally evaluated by laboratory tests that range from pragmatic simulation of use conditions to research methods designed to measure small differences and trends in the relative flammability of the materials. A method often used is the Limiting Oxygen Index (LOI) measurement. This measure is the percentage of oxygen in an oxygen-nitrogen mixture which will just support burning under specified conditions (see Volume 2 of this series of reports). A low LOI indicates high flammability. A comparison of the LOI values of some important textile materials is presented in Table 2.

Table 2 shows that the LOI values of non-fire-retarded (as is) fibers may vary by about a factor of 1.5. Since the oxygen content of air is about 21 percent, a fiber with a substantially higher LOI value will not burn in air when ignition is attempted with the material in a configuration similar to that of the test (i.e., ignited from the top with a small ignition source while essentially at room temperature). LOI values categorize materials only within the limits of those conditions under which the test is conducted (thermal flux, mode of ignition, air flow, sample size, sample shape, substrate, etc.). Thus, the test results cannot be used as an absolute measure of the fire performance of any material.

4.2 Natural Fibers

A short review of the fire safety aspects of natural fibers seems in order and approaches to reducing flammability are discussed below. Cotton is the most extensively used natural fiber. Regenerated cellulose (rayon) and cellulose acetate are modified natural fibers and are discussed among the synthetic fibers.

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TABLE 2

LIMITING OXYGEN INDICES OF SPUN FABRICS
(Fabric Weights: 4.8 to 7.0 oz/yd²)

<u>Fabric</u>	<u>LOI (% O₂)</u>
Acrilan (acrylic)	18.2
Arnel Triacetate (cellulose ester)	18.4
Acetate (cellulose ester)	18.6
Polypropylene (polyolefin)	18.6
Rayon	19.7
Cotton (greige)	20.1
Nylon	20.1
Polyester	20.6
Wool (dry cleaned)	25.2
Dynel (modacrylic)	26.7
Rhovyl "55" (polyvinyl chloride)	27.1
Nomex N-4272 (aromatic polyamide)	28.2

Data from Tesoro and Meiser, 1970.

4.2.1 Cotton

Chemically, cotton is essentially cellulose (i.e., polyanhydroglucose in which the glucose units are united by β -glucosidic linkages) and, therefore, rich in fairly reactive hydroxyl groups. In principle, cotton, in the form of fiber, yarn, or fabric, can be treated with fire retardants. The process requirements are such that fire retardant treatment of the fabric (finished) is the only commercially significant process.

4.2.1.1 Fire Retardants

Durable fire retardants are defined as those that can provide the desired degree of fire retardance for the useful life of a textile product, which can mean durability over 50 or more laundry cycles. Durability to laundering or other cleaning methods is, however, only one of several criteria a fire retardant must meet to be satisfactory and acceptable for use in fabrics for specific textile products. Other more important criteria include strength retention, avoidance of unwanted stiffness and absence of discoloration of the treated material. Criteria that can sometimes disqualify a finish are odor, sensitivity to acids or bases, and ion exchange properties. Fire retardants for cotton have been reviewed by Drake (1966, 1971). Currently, successful and potentially acceptable durable fire retardants for cotton and rayon fabrics are of two general types: metal oxides and organophosphorus compounds.

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4.2.1.1 Metal Oxides

Fire retardants based on metal oxides, especially in combination with polymeric halocarbons (chlorinated paraffins), have found greatest use in weather resistant textile products for outdoor use. Large quantities of these additives are generally needed to impart sufficient fire retardance to a fabric to enable it to pass a vertical flame test. Two techniques have been proposed for using metal oxides in laundry-durable finishes:

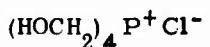
1. Formation of an insoluble titanium-antimony oxide compound within the fiber, with possible chemical attachment to the cellulose.
2. Binding antimony oxide and a chlorocarbon to the fiber with a nitrogenous resin.

There are a number of variations or modifications of these finishes (e.g., see Gulleedge and Seidel, 1950).

4.2.1.2 Organophosphorus Compounds

Organophosphorus compounds penetrate the fiber. They react, polymerize, or copolymerize with an appropriate monomer or, in some systems, with the cellulose. Another way of applying organophosphorus compounds is by depositing pre-formed phosphorus-containing polymers on the fibers or fabrics. Subsequently, these are either further polymerized or fused to provide durability. Substitution reactions without polymer formation, such as phosphonomethylation, also have been used to impart fire retardance, but with limited commercial success. Approaches that have been considered for commercialization, or have actually been implemented on a commercial scale, are described below.

Tetrakis (hydroxymethyl) phosphonium chloride (THPC)



is a white water-soluble crystalline compound: The corresponding quaternary acetate, sulfate, oxalate and phosphate salts can be prepared by substituting the corresponding acid for hydrochloric acid in the reaction with phosphine and formaldehyde. Quaternary phosphonium salts also can be prepared by reacting equimolar amounts of an acid and formaldehyde with $(\text{HOCH}_2)_3\text{P}$, i.e. tris(hydroxymethyl)-phosphine (THP). In aqueous solution, THPC exhibits acid characteristics.

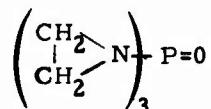
A great deal of work conducted at the U.S. Department of Agriculture Southern Regional Research Center on the chemistry and application of durable fire retardant finishes for cotton textiles, has been based on reactions of THPC and its derivatives with appropriate comonomers. A tabulation of important references may be found in Lyons (1970).

A fire retardant for medium and heavy weight cotton fabrics, based on THPC, urea, methylolmelamine and various textile modifiers, has been in use since about

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1959 (primarily in Europe). It is produced by impregnating cellulosic fabrics with the product obtained by reacting urea with THPC and then insolubilizing this compound with ammonia. The most recent THPC-based fire retardant process to become commercialized in the United States is produced by impregnating cellulosic fabrics with partially neutralized THPC and then forming a fire retardant polymer inside the fibers by reacting the methylol phosphorus compound with ammonia. This is an unusual retardant in that the chemical treatment does not reduce the strength of the treated fabrics.

Another organophosphorus compound, not used currently because of physical hazards, is tris(1-aziridinyl)phosphine oxide (APO):



Used alone it can impart fire retardance and a high degree of wrinkle resistance to cellulosic fabrics. It can also be used with THPC (Reeves, et al., 1957; Drake et al., 1961), thiourea (LeBlanc, 1965), and diammonium phosphate (Miles et al., 1960), to produce durable fire retardant finishes.

Reactive phosphonates, insolubilized on fabric either by reaction with cellulose or *in situ* polymerization, have been proposed as durable fire retardants for cotton. One compound (N-methylol dialkylphosphonopropionamide) that reacts with cellulose hydroxyl groups has attained commercial importance (Pyrovatex CP; Ciba Geigy Corp). References to these studies are listed under Aenishanslin et al., 1969; Ciba Geigy, 1965-1969; Tesoro et al., 1968. Vinyl polymerization of a vinyl phosphonate on fabric is the basis of a recently developed durable finish (Stauffer, 1973).

Many other phosphorus compounds capable of being insolubilized on fabric are documented in the literature. Among these are phosphoric triamides in conjunction with polyfunctional N-methylol compounds, dialkoxyphosphinyl triazines, diimides of alkylphosphonic acids, and others.

In general, good fire retardance is obtained on cotton fabrics through insolubilization of about 2 to 3 percent phosphorus, preferably in conjunction with nitrogen. Several excellent reviews have discussed many proposed experimental materials as well as the knowledge currently available on the mechanism of fire retardation in cellulose (Lyons 1970; Kasem et al., 1972; Reeves et al., 1974).

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4.2.2 Wool and Other Natural Fibers

Wool is basically a sulfur containing protein (Keratin). Wool textiles are generally less flammable than cellulosics, and less widely used. Thus, only limited studies are available on methods to enhance fire retardance in wool textiles (Benisek, 1972, 1972a, 1973; Friedman, 1973). The flammability of wool generally is decreased by treatment with organophosphorus compounds or with specific salts of polyvalent metals.

Flammability of fibers made from other natural protein-based polymers (e.g. silk, collagen) has not been investigated (Crawshaw et al., 1973).

4.3 Synthetic Fibers

The production of man-made fibers and natural fibers in the United States in 1973 is summarized in Table 3. All these fibers under given conditions can either ignite and propagate flame, or melt and shrink (thus exposing the wearer or contents directly to flame), or form a friable char that affords no effective protection.

TABLE 3
PRODUCTION OF NATURAL AND MAN-MADE FIBERS IN THE
UNITED STATES IN 1973

<u>FIBER</u>	<u>AMOUNT PRODUCED (billion lb)</u>
<u>Natural*</u>	
Cotton	3.65
Wool	0.17
<u>Man-Made**</u>	
Rayon	0.89
Acetate	0.46
Nylon	2.18
Polyester	2.77
Olefin	0.42
Acrylic	0.74
Glass	0.69
Other	0.13

* Reference: USDA Economic and Statistical Analysis Division, Textile Highlights, American Textile Manufacturers Institute, Inc., Washington, D. C., December, 1973.

** Reference: Textile Organon (January-February, 1974), Textile Economics Bureau, Inc., New York.

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4.3.1 Fire Safety Aspects of Synthetic Fibers

Some general comments on the fire retardance of synthetic fibers are presented below. Additional information may be found in Section 4.5.

4.3.1.1 System Aspects of Textile Flammability

System design of a textile construction is often effective in reducing fire risk. This approach can be illustrated by two examples:

1. Carpets of unmodified acrylic, nylon or polyester face fiber can be made to resist ignition by a cigarette, fireplace ember, or the standard methenamine fuel tablet, *inter alia* by: (a) increasing the weight of the face fiber by a few ounces per square yard; (b) using hydrated alumina as a heat absorbing filler in the carpet backing; or (c) applying a heavier and more even coating of backing adhesive.

2. When the unmodified thermoplastic fibers in this group resist ignition, it is because they melt away from the ignition source. If ignited, they frequently self-extinguish because the molten polymer drops away from the flame front. To take advantage of this phenomenon, one must: (a) avoid using these fibers in proximity to non-melting fibers (e.g., cotton, rayon, or acrylic); (b) avoid the use of non-melting sewing thread; (c) determine whether the fabric, given a specific construction and weight, will drip out upon ignition (heavier fabrics, for example, may not drip out, whereas the same fiber compositions may do so when used in light fabrics).

4.3.1.2 Chemical Modifications For Fire Retardance

Chemical modifications are introduced to promote fire retardance by:

1. Altering the course of the thermal oxidative degradation of the polymer that supplies the volatile fuel to ignite and propagate flame (this effect may be accomplished by chemical modification of the polymer that increases the amount of char formed or by causing a protective char barrier to isolate the polymer from the flame);
2. Emitting free-radical-trapping and/or energy-absorbing fragments into the volatile fuel, thus cooling or quenching the flame reactions;
3. Accelerating the decrease of viscosity of the polymer at the flaming surface, thus promoting drip-out.

Chlorine, bromine, phosphorus, nitrogen, sulfur, boron, and antimony play dominant roles in the chemical modification of flammability properties of polymers from which synthetic fibers are formed (Lyons, 1970). Fire retardant compounds and additives are discussed in Section 4.7. These flammability-modifying elements can be incorporated into fibrous structures in many ways, including:

1. Monomeric building blocks containing one or more of these elements can

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be incorporated directly into the polymer chain (e.g., vinyl bromide can be copolymerized into a modacrylic).

2. The polymer can be modified by grafting (e.g., vinyl chloride can be grafted onto preformed poly(vinyl alcohol)).

3. An additive can be incorporated into the polymer solution or melt before extrusion into fiber form (e.g., hexaproxy phosphotriazene can be introduced into viscose dope prior to extrusion to form rayon).

4. The textile material (fiber, yarn or fabric) can be treated topochemically with reagents from solutions or emulsions (e.g., brominated alkyl phosphate may be sorbed onto polyester, or THPC with a coreactant onto rayon). These approaches are organized schematically in Figure 1.

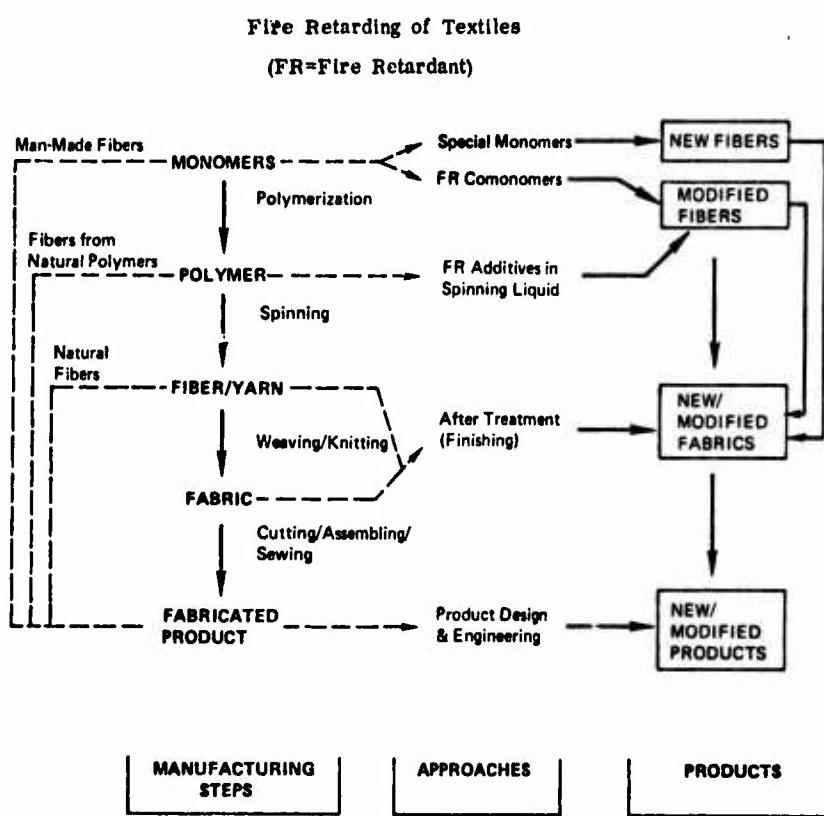


Figure 1

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While certain desired effects can be attained by use of the chemical reagents and processes described above, the mechanisms of their effectiveness are largely unknown. Only working hypotheses are available. Of the above cited chemicals, some are postulated to play the role of chain stopper, char barrier former, or drip promoter. A given retardant composition often produces different degrees of effectiveness in different polymers.

4.3.1.3 Durability of Fire Retardant Modifications

Fire retardant variants cited in the following sections will exhibit different durabilities to repeated laundering. Important factors in laundering are water hardness, the chemical nature of detergent and soap formulations, bleaches and exposure to sunlight. The mechanisms of deterioration of fire retardance may differ from one fiber formulation to another, e.g., hard water deposits that accumulate when low phosphate detergents are used will destroy the effectiveness of topochemically processed rayon when the retardant is based on phosphorus or nitrogen. Alkaline detergents may surface-saponify cellulose acetate, thus forming the equivalent of a non-thermoplastic cellulose wick to stabilize a flame and prevent drip-out.

4.3.2 Regenerated Cellulose and Cellulose Acetate

Both regenerated cellulose and cellulose acetate derived from cellulose, a natural polymer, are best included among the synthetic fibers. The term "regenerated cellulose" describes cellulose that has been dissolved in the form of a soluble derivative and subsequently reprecipitated. Regenerated cellulose fiber is known as "viscose" or "viscose rayon", while regenerated cellulose film is known generically as "cellophane". Cellulose acetate and triacetate are modified (esterified) cellulose.

4.3.2.1 Rayon

Unmodified rayon ignites readily and burns rapidly to completion. Fire retardant treatments for rayon encompass all the means available for treatment of cotton (see Section 4.2.1). In addition, it is possible to incorporate effective additives into the viscose spinning solution prior to extrusion. One such additive, used in a commercial product is an alkoxy phosphazene that remains dispersed in the fiber and shows excellent durability (Godfrey, 1970).

Appreciable quantities of nonwoven, disposable textile items are produced from rayon. Because they are not laundered for reuse, it is possible to achieve fire retardance with approximately 20 percent loading of water soluble salts (e.g., ammonium sulfamate or diammonium phosphate).

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4.3.2.2 Cellulose Esters

The unmodified cellulose ester fibers (mainly cellulose acetate and triacetate) ignite and propagate flame. The fabric drips while continuing to burn.

The principal method used to achieve fire retardance in cellulose esters is to incorporate a brominated alkyl phosphate ester into the spinning solution before extrusion. The fire-retarded product either resists ignition or the affected portion melts and drips out at once.

4.3.3 Polyesters

The most important polyester fiber is poly(ethylene terephthalate). (see Section 6.3.8). While poly(ethylene terephthalate) is flammable, many polyester textiles will not ignite because the fabric melts away from a small ignition source or self-extinguishes by drip out. Both of these mechanisms will fail with heavier constructions or if even only a small amount of non-thermoplastic fiber (e.g., cotton) is present (see Section 4.6).

To improve fire retardance in heavier weight constructions, it is possible to use several approaches (see Section 4.3.1.2). For example, the molecular composition of poly(ethylene terephthalate) can be altered to contain bromine by using 2,5-dibromoterephthalic acid to replace some of terephthalic acid, or by using bis(hydroxyethoxy)tetrabromobisphenol A to replace some of the ethylene glycol. Antimony oxide then can be included in the formulation to enhance the effectiveness (Textile Industries, 1973). Bromine can also be introduced by means of an additive incorporated during the melt spinning process, or it can be applied to the finished fabric using an aqueous emulsion of tris(2,3-dibromopropyl) phosphate.

The comfort and aesthetics of poly(ethylene terephthalate) can be enhanced significantly by blending it with cellulose acetate or triacetate. When cellulose acetate contains appropriate fire retardants, or when fire retardants are topochemically applied to the blend fabric, good fire retardance can be obtained for some fabric constructions.

4.3.4 Nylon

Nylons are polyamides (see Section 6.3.5). The unmodified polyamides, nylon 6, nylon 66, nylon 610, etc., perform essentially like unmodified polyester with respect to flammability. Nylons resist ignition and flame propagation in vertical configurations because of drip-out, except in heavier weight fabrics. Carpets with nylon face fiber readily pass the methenamine fuel tablet test (see Volume 2) with even less face fiber density than poly(ethylene terephthalate). Nylon blends with cellulosics represent a flammability hazard (see Section 4.6). Published means for

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improving nylon fire retardance have serious deficiencies. Four basic approaches for obtaining nylon fabrics with reduced flammability have been cited (Stepniczka, 1973). Each method impairs some other desirable attribute (e.g., performance, durability or economics). One frequently cited approach (Douglas, 1957) consists of applying a finish of thiourea/formaldehyde resin; experimental evidence shows that this formulation may work by accelerating nylon degradation and promoting drip-out, but laundering durability is impaired.

4.3.5 Acrylics and Modacrylics

Acrylics are polymeric fibers containing at least 85 percent polyacrylonitrile. Modacrylics (modified acrylics) are copolymers of acrylonitrile with vinyl chloride, vinylidene chloride, and/or, possibly, other vinyl monomers. Acrylic fibers must not be confused with acrylic plastics, which do not contain acrylonitrile.

Acrylics shrink away from a small ignition source and therefore escape ignition. Once ignited, however, acrylics burn vigorously, ejecting plumes of flaming gases and dense smoke. The rapid heat generation is due in part to a spontaneous "zipper-like," highly exothermic, cyclization reaction between adjacent nitrile groups. Acrylics are made acceptable for the carpet pill test by blending the face fiber with 20 percent of modacrylic fiber. Any other attempts to improve flammability require copolymerization of acrylonitrile with a sufficient amount of other monomers to place the product among the modacrylics.

Modacrylics suffer from certain shortcomings in textile performance. Historically, they have a low softening point and poor thermal dimensional stability although some improvements have been made. These fibers find acceptance in children's sleepwear because they are relatively inexpensive, resist ignition, and burn slowly or self-extinguish if ignited.

The fire safety characteristics of modacrylics can be enhanced by copolymerizing with vinyl bromide. This does not impair the fiber properties and may even improve them. In one commercial application, antimony oxide also is present. The fire retardance is sufficiently good so that fabrics are being promoted that contain up to one-third polyester along with the vinyl bromide-containing modacrylic copolymer.

Allyl or vinyl esters of phosphoric or phosphonic acids are being offered as comonomers for incorporation into modacrylics, e.g., bis(2-chlorethyl) vinyl phosphonate. Addition of tricresyl phosphate or tris(dibromopropyl) phosphate to spinning solutions also are possibilities for improving fire retardance, but no commercial use of this concept is known to date.

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4.3.6 Poly(Vinyl Chloride) and Poly(Vinylidene Chloride)

Poly(vinyl chloride) (PVC) fibers as such can be considered to be inherently and permanently fire retarded (see Section 6.3.3) by virtue of their high chlorine content (Collins, 1972). As a textile fiber, PVC has exhibited poor aesthetics and poor dimensional stability, but an improved heat- and solvent-resistant syndiotactic form of PVC has recently been developed in Italy. Raising the chlorine level by copolymerization with vinylidene chloride (see Section 6.3.12) adds to the desired fire retardant effect. Antimony oxide as a synergist also has been used.

Saran filaments (see Section 6.3.12 on Vinylidene Chloride Polymers) offer high strength and flexibility and are chemically resistant and self-extinguishing. The mono-filaments have been widely used in automotive seat covers, outdoor furniture, agricultural shade cloth, filter fabrics, insect screening, window awning fabrics, venetian blind tape, and brush bristles. Extruded multifilament yarns have been used for draperies, upholstery, doll hair and other wigs, dust mops, and various industrial fabrics.

A Japanese product, Cordelan, is formed by graft polymerizing PVC onto poly(vinyl alcohol) (PVA) (Collins, 1972). Fibers from this bicomponent polymer are resistant to ignition. They have a pleasant hand and dye readily, but shrink severely in hot-wet exposure. They tolerate blending with 20 percent cotton without becoming flammable.

4.3.7 Polyolefins

Polyolefin fibers are polyethylene or polypropylene. (see Section 6.3.1). These fibers ignite readily and continue to burn with flaming drops. No successful formulas are known that retard the flammability of polyolefin fibers. The use of retardants such as tris(dibromopropyl) phosphate and aliphatic chlorine compounds/antimony oxide have been cited.

4.3.8 Polyurethanes

Polyurethanes are used in elastomeric fibers, principally for stretch garments. Polyurethane is used as a coating for "wet-look" lightweight durable fabrics although no effort is known to achieve fire retardance. If such interest should arise, a starting point for development might be found in the urethane foam technology that has been reviewed by Papa (1970, 1972) who cites numerous halogen and phosphorus formulations of both the additive and reactive type.

4.4 Inorganic Fibers

Fibers can be made from inorganic glasses and from synthetic inorganic polymers.

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4.4.1 Glass Fibers

For some end uses, glass fibers are important. They melt at about 815°C, but do not burn. They are generally treated with organic finishes to enhance their resistance to abrasion and to improve other functional properties. The flammability hazard of glass fibers in actual use can be significantly increased by increasing the presence of these surface modifying organic materials. Fabrics made from glass fibers are used widely in various industrial applications, in composites and laminates and in draperies and curtains.

Other nonflammable inorganic fibers (e.g., asbestos, quartz, silica, alumina) are produced in small volumes for highly specialized applications. Glass and other inorganic fibers may pose health hazards (silicosis, asbestos).

4.4.2 Fibers From Inorganic Polymers

Synthetic inorganic polymers (e.g., polymers with phosphorus-nitrogen backbones and little or no carbon) can now be made and some are discussed in Section 5.3.9. Fibers do not appear to have been made by this approach except, perhaps, experimentally.

4.5 Fibers From Thermally Stable Synthetic Polymers

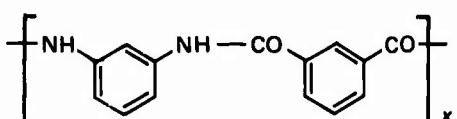
An important approach to fire retardant synthetic fibers may well be utilization of some of the relatively new classes of thermally stable synthetic polymers with backbones containing some nitrogen. These new thermally stable polymers may be formed into fibers that are resistant to long-term heating and, in many instances, burning.

At this time, many of these polymers are expensive. Regulations can be expected, however, to require the use of flame resistant textiles in many additional areas including mass transit (air and ground). It can then be expected that modern chemical technology will be called on to provide lower cost approaches to thermally stable polymers. This section is limited to a review of those stable polymers that are available or may soon become available as fibers.

Thermally stable synthetic fibers offer certain advantages over inorganic fibers. They have lower density, greater elongation, superior abrasion resistance, higher strength-to-weight ratios (in some cases), and can be formed into wider ranges of filament and yarn diameters. Current or modified fiber-forming techniques can be used in their manufacture.

4.5.1 Aromatic Polyamides (Aramids)

This polymer system is the basis for the first commercially available thermally stable aromatic polyamide fiber, Nomex®



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(poly(m-phenylene isophthalamide)) is duPont's first version of this class of polymers. Nomex® decomposes at about 370°C. Fabrics woven of the undyed material are more resistant to burning than solution dyed material (Ross, 1973). In low-thermal environments involving a small ignition source, Nomex® is self-extinguishing; however, when exposed to a large heat flux, it will shrink, burn, and propagate flame to other materials. As described below, improvements can be made by treating the woven or knitted form of the material. In comparison with other commercial fabrics, the Limiting Oxygen Index (LOI) of Nomex® is higher than most; however, its LOI is the poorest of the thermally stable fibers discussed in this section. An improved version, HT-4, ranks with the best of the thermally stable fibers. A comparison of LOI values is presented in Table 4.

TABLE 4

LIMITING OXYGEN INDICES OF HIGH PERFORMANCE FABRICS
(Fabric Weight: 4.5 - 7.0 oz/yd²)

<u>FABRIC</u>	<u>LOI (%O₂)</u>
Untreated Cotton	16-17
F. R. Treated Cotton	31-32
Natural Nomex®	27-28
Dyed Nomex®	25-27
Kynol®	29-30
Fypro®	29-30
Durette®	35-38
PBI (polybenzimidazole)	38-43
Nomex® HT-4	42-46
PBI-S	42-49

Source: Coskren, 1973; DuPont, 1976.

Nomex® offers excellent strength, wear, hand and chemical and solvent resistance. Its strength is virtually independent of the rate of extension. This is of great importance when a high rate of loading is a critical parameter, such as is encountered in transmission and safety belts, parachutes and tires. Moreover, gamma radiation causes an increase in strength of Nomex® at elevated temperatures (Ross, 1962), whereas aliphatic polyamide and polyester fibers are severely degraded when exposed to gamma radiation.

Nomex® currently is being used in military clothing, race drivers' garments, hospital bedding, filtration bags, various forms of transmission belting, industrial protective clothing, and (to a minor degree) children's sleepwear. Staple Nomex® formed into paper is being used as electric motor insulation and as honeycomb core for aircraft wall panels. Potential future applications in aircraft interiors, parachutes and carpeting depend on improving color fastness.

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An aromatic polyamide fiber with a structure similar to that of Nomex® has been produced by Monsanto. This product, Monsanto X-500®, has properties equivalent to those of Nomex® in all respects. (Ross and Opt, 1967; Opt and Ross, 1969). Fenilon (phenylon) fiber, developed in the Soviet Union also has thermo-mechanical properties similar to those of Nomex®. It has recently been reported that another aromatic polyamide (Sulfon T) has been developed in the Soviet Union. It has better thermomechanical properties than those of Nomex® and utilizes monomers containing the para-linkage in the aromatic polyamide rather than the meta-linkage; much higher tenacity and modulus have been attained (Preston, 1970). The thrust in the development of a more recent aramid, of Kevlar®, has been directed toward the production of high modulus fibers for use as reinforcement in structural composites and tires. Tenacities in the 19-22 g/d range, with a rupture elongation of 3 to 4 percent, have been reported for Kevlar 29® (Rothuzer, 1973) and the same tenacity with 2 to 3 percent elongation for Kevlar 49®. This tremendous gain in tenacity, coupled with densities of 1.40 to 1.45 g/cm³, provides a potential replacement for glass, steel, nylon, and polyester fibers now used as tire cord, provided the new materials can be made at a competitive cost.

Tensile tests at various temperatures show that both Nomex®, Kevlar 29®, and Kevlar 49® fibers retain 50 percent of their initial strength after 30 minutes at 270°C. By various modifications, a fiber (labeled HT-4) has been produced that does not burn or shrink in air. The fabric yields more smoke than Nomex® or Kevlar® when exposed to flames. This modified fiber is reported to be intended for military protective clothing.

4.5.1.1 Chemically Treated Aromatic Polyamides

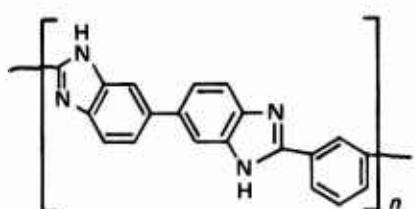
The Durette® fibers form a family of chemically treated aromatic polyamide woven and knitted fabrics. Durette-400® contains about 5 percent chlorine and is self-extinguishing in NASA's vertical burn, bottom ignition test (Federal Test Standard 191 Method 5903). However, when a calrod heater is held against the fabric it will ignite after 2.5 seconds at 895°C (Coskren, 1973). It does not shrink or melt on exposure to flame and does not split if the edges are restrained. Durette-400® has been extensively tested for flammability in oxygen-rich environments (Ross, 1973) and has shown improved flammability performance when compared to Nomex®. It has been worn by the astronauts in Skylab missions.

Fypro® is essentially chemically treated Nomex®. It is charcoal black and self-extinguishing; but when held against a calrod heater, the fabric will ignite when the temperature reaches between 840 to 870°C. It does not shrink excessively, and remains soft and flexible after exposure to 452°C. The material has also been evaluated in garment form, where its abrasion and wear resistance have been poor. These modified aromatic polyamides fall short in color, strength, UV sensitivity, and cost.

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4.5.2 Polybenzimidazole Fibers

Polybenzimidazole (PBI) fibers are prepared from a diester of isophthalic acid and diaminobenzidine:



The polymer is spun from a solvent using typical dry spinning techniques. The initial objective was to obtain a material having long-term thermal stability at temperatures above 500°C, but extensive evaluation of fiber, yarn and fabric demonstrated that PBI did not have the desired long-term thermal stability (Opt and Ross, 1969; 1967). Von Krevelen (1972) confirmed that the maximum long-term use temperature was only 250 to 300°C. Measurements of burning rate in air and oxygen indicate that this fiber will not burn under the conditions of these tests (Ross, 1973; Coskren, 1973; Von Krevelen, 1972; Ross, 1971). This characteristic, in combination with high moisture regain (13 percent compared to 8.5 to 10.3 percent for cotton), has resulted in extensive studies of PBI for clothing and related applications where comfort and fire safety are important requirements.

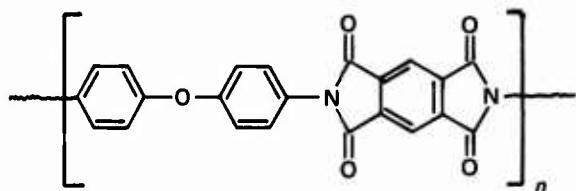
The mechanical properties, durability, and protective capability of PBI in fabric form have been demonstrated through laboratory and field evaluation of fabrics, aircrew protective clothing, as well as personnel parachute packs and harnesses. One of the early problems of PBI fabric was the tendency to shrink excessively when exposed to a large flame that would engulf the entire sample or garment. To overcome this shrinkage, a treatment was developed that produced fiber (PBI-S) with less than 5 percent shrinkage under these conditions. Initial efforts to dye PBI fiber have resulted in some successes; however, the natural color (light brown) precludes use of any but medium to dark shades. Among the major shortcomings of PBI are its cost. Since this is related to monomer costs and production quantities, it can be concluded that, if PBI is produced in sufficient quantities, the cost will be more competitive with that of other flame resistant fibers.

4.5.3 Aromatic Polyimides

Aromatic polyimides are synthesized from an aromatic dianhydride and an aromatic primary diamine. They are used primarily for moldings, composite matrix resins, films and foams. The films are the best non-halogenated fire resistant films available. They are clear, amber colored, fairly flexible, and have high tensile strengths. Fibers have been spun from polyimides and their mechanical properties

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have been investigated exhaustively. A typical polyimide repeat unit is poly(oxydiphenyl pyromellitimide)(Kapton®):

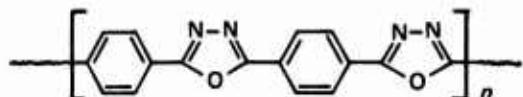


Various woven forms of at least one polymide fiber have been characterized thoroughly. PRD-14, a fiber spun from the above polymer, demonstrated excellent thermal aging characteristics (Opt and Ross, 1969; Ross, 1967). Like Nomex® and PBI, this fiber was unaffected by gamma radiation; however, UV degradation was more rapid than for either PBI or Nomex®. The PRD-14 fabrics were reasonably flame resistant in air, but this may have been attributable to the weight of the fabric evaluated. In oxygen-rich environments, PRD-14 burns at a considerably faster rate than Nomex®.

Kermid® is a French fiber, reported to be a polymide and "inherently fire resistant." The Russian Arimid® is said to be a polyimide. Aromatic poly(amide-imide) fibers, e.g., the French Kermel® and Japanese Paifron® also are reported (Pigeon, 1970).

4.5.4 Other Heteroaromatics

A variety of thermally stable, high-char-forming heteroaromatic polymers have been studied, primarily as matrix resins for composites. A number of these polymers have been formed into fibers. Polyoxadiazole (PODZ) has been formed by dry spinning the polyhydrazide precursor polymer from dimethyl sulfoxide followed by thermal cyclodehydration to form the final structure (Drake, 1971):

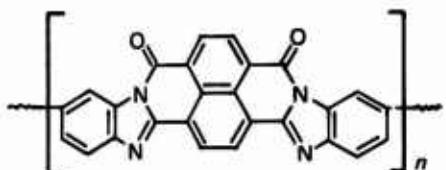


Although long-term thermal stability of these fibers was superior to PBI (Preston, 1970; Black, 1970), they were found to be extremely sensitive to light (Opt and Ross, 1969). The hydrazides and triazoles (Preston, 1970; Black, 1970; Gloor, 1968) reportedly are inferior to the polyimides and polybenzimidazoles. Teijin has recently introduced an aromatic polyamide that, upon heating or exposure to flame, produces a flame-resistant poly(amide-benzimidazole) structure (Preston, 1970).

The most recent and most promising candidate in the high-temperature polymeric textile fiber field is poly(bisbenzimidazobenzophenanthrolinedione), labeled

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"BBB" (Van Deusen, et al., 1968; Gloor, 1969):



When tested at 642°C the fibers retained 60 percent of their room temperature tenacity. Usable strengths may exist well above 697°C. This fiber is not flammable. Disadvantages at this time are primarily cost and color.

Other systems, such as pyrrones and quinoxalines, can be formed into fibers, but it is doubtful that they would have much to offer over PBI and probably would be even more expensive.

4.5.5 Phenolic Fibers

Only one phenolic fiber, Kynol® has been developed. In its preparation a phenol-formaldehyde polymer is first spun into multifilament yarns and is then crosslinked or cured with formaldehyde (Von Krevelen, 1972). The cured Kynol® fiber is light yellow, but can be bleached to a pure white. The strength of the fiber is low, as is its abrasion resistance. When exposed to flame, the fiber chars on the surface, retaining its shape with no distortion. Its LOI is superior to that of Nomex® (Coskren, 1973) and the fiber is resistant to thermal shrinkage. Because of its poor abrasion resistance, Kynol® is blended with other fibers to effectively utilize its flame resistance and thermal stability. Felt and batting made of Kynol® have potential for providing both insulation from cold and protection from fire in cold weather garments. Although raw material costs are low, processing will be costly until the manufacturing process is scaled up to larger volumes.

4.5.6 Carbon and Graphite Fibers

Carbon and graphite fibers have been the subject of extensive research since 1963 and are currently available in fiber, yarn, tow, and fabric forms (Drake, 1971). Their primary applications have been as reinforcement in structural and ablative composites; these applications capitalize on the high modulus and, in some forms, high tensile strength of these fibers. Graphite fibers have decreased sharply in cost, depending on the yarn size and quantity desired. Production exceeds 100,000 pounds per year. With the development of continuous processes for converting petroleum pitch to carbon fibers, it is anticipated that costs may be appreciably lowered at higher production volumes.

Poor abrasion characteristics, low elongation, brittleness, and black color almost completely preclude the use of carbon fibers in textile applications unless new techniques for blending them with other more ductile fibers can be developed.

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Carbon cloth should be less expensive than graphite fabrics as the preparation is less critical and the precursor can be processed in fabric form. Blends of carbon and glass yarns have been prepared for applications that require electrically conductive fabrics. Their life is limited, however, primarily because of the poor flexibility of the carbon component. Future development of either flame resistant or thermally stable finishes to provide lubricity may lead to improved life.

4.5.7 Chelated Polymers

Chelated polymers containing certain metals have been formed into fibers that have excellent flame resistant properties (Von Krevelen, 1972). The fiber, Enkatherm® is stable even when exposed to flames at 1500°C. It can be spun-dyed, with color being obtained through the use of specific chelating ions, but white or natural color cannot be attained.

4.5.8 Fluorocarbon Fibers

Fibers based on polytetrafluoroethylene or chlorotrifluoroethylene have been prepared. Typical of these is Teflon®. While these fibers have the fire resistance properties of the fluorocarbon polymers, they also have a number of limitations, including high density, low strength, poor abrasion resistance, poor dyeability, excessive softening at elevated temperatures and high cost. Their major use has been in applications such as valve packings and bearings that require chemical resistance and a low friction coefficient. These fibers are obtained mainly in the form of continuous filament yarn and have found some use in conjunction with other materials.

4.6 Fire Safety Aspects of Fiber Blends

Fabrics made of yarns containing two or more fibers of different chemical compositions and properties have attained great commercial importance in textile markets. The technology of these blends has become an important illustration of the textile industry's skill in the optimal utilization of available fibers for the manufacture of new or improved products. The fire safety aspects of blend fabrics have received attention only since about 1969, as a consequence of regulations and industry wide activity on general textiles fire safety problems.

Fiber blends pose special fire hazards. For example, care must be taken to avoid the presence of nonthermoplastic components in any blend of thermoplastic fibers. Even cotton sewing thread should be avoided because it may serve as a wick to stabilize the flaming melt (see Section 4.3.1.1). Early investigations have established that the fire safety aspects of blends cannot be predicted from a knowledge of the behavior of individual fiber components (Tesoro and Meiser, 1970). In effect, a blend becomes a new chemical entity with flammability properties of its own.

Fire retardant systems that are effective on a specific fiber do not necessarily

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provide useful approaches to the treatment of blends. Physical and chemical interactions of different fibers in blends under conditions of burning pose complex problems that are not understood and have not been studied adequately. However, a considerable amount of empirical work has been carried out during the last few years on the flammability of blends and is reviewed below briefly.

4.6.1 Blends of Fibers Made From Thermally Stable Polymers

Availability (or potential availability) of fibers with satisfactory textile properties made from thermally stable polymers (see Section 4.5), such as aromatic polyamides, and the issuance of new flammability standards, have lead to experimentation with varying amounts of these fibers in blends. These investigations offer interesting challenges, but prediction of the fire safety characteristics of these blend materials is extremely difficult and generalizations are not possible. Results depend primarily on the chemical composition of specific fibers combined in the blend as well as on the geometry of the material tested in addition to the nature and conditions of the test employed. At this time, it is not clear whether significant developments have resulted from this approach. The assumption that the thermally stable fiber could play the role of a fire retardant material, and decrease the flammability of combustible fibers to which it is added, is clearly not warranted. Nevertheless, pragmatic investigations of this nature are justified by the assumption that cost, as well as outstanding fire safety characteristics of thermally stable fibers, might be "diluted" through use of conventional fibers in blends to obtain textile products that would be economically attractive yet which still exhibit satisfactory performance properties and a level of fire retardance sufficient to meet the standards prescribed for a given end use.

The flammability of fabrics made from blends of the aromatic polyamide Nomex® with some combustible fibers has been examined experimentally (Tesoro and Rivlin, 1971). The LOI for blends of Nomex® with polyester and with cotton was found to be lower than the average of the oxygen indices of the component fibers. The fiber composition for a contemplated application in textile products would depend primarily on considerations of processing ease, fabric performance properties, and flammability behavior of the fabric in tests specified by the standards covering its end-use. Fabrics made from blends of Nomex® with fire retardant fibers generally exhibit high LOI values and self-extinguishing behavior in vertical fabric flammability tests. Results have been reported for blends of Nomex® with a modacrylic and with a fire retarded rayon (Tesoro and Rivlin, 1971).

Some data are available for blends of Kynol® with other fibers. For example, the relationship of oxygen index to Kynol® content for Kynol®/wool blends indicates that "nonflammable" mixtures are obtained for Kynol® contents above 35 percent (Porczynski, 1970).

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4.6.2 Blends of Synthetic Fibers

The objective in evaluation and development of blends of fire retarded synthetic fibers is quite different from that outlined above for blends of thermally stable fibers. While the incorporation of more economical fibers, even if combustible, might be examined to decrease cost, the primary purpose would be development of products in which ease of processing, satisfactory performance properties, and fire retardance can be combined to yield attractive textile materials. Possibilities are numerous, and the spectrum of properties to be considered for various end-uses is wide. However, only a few examples of blends considered to be candidates for fire retarded fabrics can be given since few results can be extracted from the technical literature.

Blends of synthetic fire retarded fibers may yield thermoplastic or nonthermoplastic products. In the former instance, the difficulty in evaluating the intrinsic flammability of products permit conclusions only with regard to the performance of a specific fabric or product in a specific test. For example, fabrics made from blends of polyester with fire retarded acetate or triacetate have been developed to meet specific flammability standards and can be described as fire retarded only when nonthermoplastic components are absent.

In the case of nonthermoplastic fire retarded fibers, e.g., fire retarded rayon, flammability behavior in blends with other fibers can be compared more easily. For example, data obtained on blends of PFR® rayon with other fire retarded fibers have shown that a range of fire retarded compositions can be obtained (DeFosse and Harrison, 1972). Their commercial possibilities would be determined by performance properties and economics.

Fire retarded fabrics for specific uses have been obtained from blends of wool with PVC fibers and with modacrylic fibers. Fabrics made from 60/40 wool/PVC yarn have been reported to exhibit satisfactory properties and to pass the vertical flammability test prescribed in the children's sleepwear standard (DOC FF-3-71) (Benisek, 1973).

4.6.3 Polyester/Cellulose Blends

A discussion of fiber blends in textile products would not be realistic without consideration of polyester/cellulose blends, and of polyester/cotton blends in particular, since these represent by far the most important type and the largest volume in the total market for blend fabrics. They are used extensively in most items of apparel and in many home furnishings. In many cases, it is difficult to visualize their replacement by other fiber compositions. The state of the art on the problems of fire retardance in polyester/cellulose blends has been reviewed by Tesoro (1973).

4.7 Fire Retardant Compounds and Additives

A brief summary of fire retardants primarily used in textile applications is

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presented in this section. Further information may be found in Section 6.2.

Recent books on fire retardants include extensive discussion of most compounds suggested as fire retardants for polymeric materials (Lyons, 1970; Kuryla and Papa, 1973). Summarized also in these treatises are current thoughts and speculation on the mode of action of fire retardants in polymers.

Generally, the flammability of polymers can be decreased by altering the products of thermal decomposition so that (1) nonflammable combustion products are formed at the expense of flammable volatiles (solid phase retardation), (2) interference results by trapping free radical species in the gas phase, or (3) a combination of these effects occur. Most experimental observations can be explained with reference to these mechanisms of fire retardation. Other modes of action include the following (Kuryla, 1973):

- (1) Noncombustible gases are generated that dilute the oxygen supply and tend to exclude oxygen from the polymer surface.
- (2) Radicals or molecules from retardant degradation react endothermally or interfere with chain reactions in the flame or substrate species.
- (3) The retardant decomposes endothermally.
- (4) Nonvolatile char or liquid barriers are formed that minimize oxygen diffusion to the condensed phase and reduce heat transfer from flame to polymer.
- (5) Finely divided particles reduce flame propagation by altering the course of gas phase reactions leading to less reactive radicals.

The most useful types of fire retardant compounds are reviewed briefly below with respect to chemical type, important applications and effectiveness.

4.7.1 Fire Retardants Based on Phosphorus

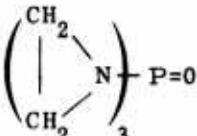
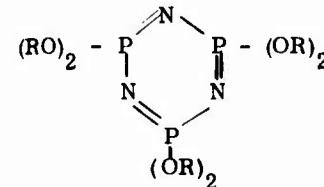
Phosphorus compounds have been used extensively for decades as fire retardants for cellulosic polymers. Ammonium phosphates were among the first compounds found to inhibit the combustion of wood or cotton (Little, 1947). Polyphosphoric acids, ammonium polyphosphates and other salts and complexes of nitrogenous compounds with phosphoric acid are still commercially important for applications in which durability to leaching and laundering is not required (e.g., disposables).

For application in which insolubilization of the phosphorus is needed to attain durability (e.g., textiles), reactive organo-phosphorus compounds of high phosphorus content have been developed. The most important among these compounds have been used primarily for cellulosic fibers and are identified in Table 5 with their textile applications.

These phosphorus compounds are insolubilized through reaction with hydroxyl groups, polymerization, or copolymerization *in situ*. They are frequently (but not necessarily) effective in the solid phase (i.e., they alter the products of thermal decomposition and suppress the formation of combustible volatiles). Phosphorus compounds also inhibit glowing.

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TABLE 5
REACTIVE ORGANOPHOSPHORUS FIRE RETARDANTS

<u>Compound</u>	<u>Type</u>	<u>Major Applications</u>
$(\text{CH}_3\text{O})_2 \text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{OH})$	phosphonate	Cotton fabrics
$(\text{RO})_2 \text{P}(\text{O})(=\text{CH}_2)$	phosphonate	Cotton fabrics
$(\text{HOCH}_2)_4 \text{P}^+ \text{Cl}^-$	phosphonium salt (THPC)	Cotton fabrics Wool fabrics
	phosphoric triamide (APO)	Cotton fabrics
$(\text{CH}_3\text{NH})_3 \text{P} = \text{O}$	phosphoric triamide	Cotton fabrics
	phosphazene	Rayon fiber

4.7.2 Fire Retardants Based on Halogens

Halogen-containing fire retardants are used extensively for fibers and textiles in several ways. Halogenated monomers and comonomers are used in the manufacture of poly(vinyl chloride) fibers, modacrylic fibers, and poly(vinyl chloride)/poly(vinyl alcohol) bicomponent fibers. Typical of fire retardants in this class are: vinyl chloride, vinylidene chloride, vinyl bromide, and (possibly) other halogenated vinyl monomers. Halogenated comonomers also have been used in the condensation polymerization reactions leading to polyester formation (e.g., poly(ethylene terephthalate) modified with 2,5-dibromoterephthalic acid or with bis(hydroxyethoxy)tetrabromobisphenol A).

Halogenated nonreactive compounds have been incorporated as additives in the manufacture of fire retarded rayon, acetate, triacetate, and polyester. Finally, chlorinated paraffin waxes, PVC and PVB latices have been used for finishing of industrial and military fabrics (e.g., tentage) where high add-ons can be tolerated and durability to leaching is needed, but durability to washing is not required.

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Halogenated compounds are believed to achieve their effectiveness primarily through vapor phase mechanisms that inhibit oxidative reaction in the flame. They are often used in conjunction with antimony trioxide, which interacts synergistically with the halogen. Important halogen-containing flame retardants used in fibers and textiles are summarized in Table 6.

TABLE 6
HALOGEN CONTAINING FIRE RETARDANTS

<u>Halogen Compounds</u>	<u>Mode of Use</u>	<u>Proposed Applications</u>
Vinyl chloride $\text{CH}_2 = \text{CHCl}$	Monomer or comonomer in manufacture of fibers	PVC fibers Modacrylic fibers PVC/PVA fibers
Vinyl bromide $\text{CH}_2 = \text{CHBr}$	Comonomer in manufacture of fibers	Modacrylic fibers
2, 5-Dibromoterephthalic acid $(\text{Br})_2 \text{C}_6 \text{H}_2 (\text{COOH})_2$	Comonomer in modified poly(ethylene terephthalate)	FR polyester fibers
Bis(hydroxyethoxy)-tetrabromobisphenol A	Comonomer in modified poly(ethylene terephthalate)	FR polyester fibers
Tris(2, 3-dibromopropyl) phosphate	(a) Additive in fiber manufacture. (b) Finishing of fabrics from 100% polyester.	FR acetate fibers FR triacetate fibers FR polyester fabrics
Chlorinated paraffin wax, PVC latex, PVB latex	Fabric finishing	Industrial and military fabrics

4.7.3 Fire Retardants Based on Boron Compounds

Boron compounds have been used as fire retardants, primarily for wood and chiefly in the form of inorganic salts; however, temporary (non-durable) fire retardant treatments based on specific mixtures of borax and boric acid have been recommended for cotton and cellulosic fabrics (Little, 1947). Even in applications where durability is not needed, the boric acid/borax treatments have now been abandoned in favor of those based on phosphates since boron-based fire retardants do not suppress after-glow and are therefore less effective in reducing hazard.

4.7.4 Synergism and Synergists

Synergistic interaction of elements and compounds that impart fire retardance to polymeric substrates have been discussed by Lions (1970) and Weil (1975). Hindersinn and Witschard (1975) have reviewed phosphorus/halogen synergism.

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Critical examination of the literature leads to the conclusion that few generalizations are valid regarding true synergistic interactions of fire retardants.

Antimony/halogen synergism is significant, and has been attributed to formation of volatile antimony halides in burning, but the relative importance of vapor phase and solid phase action of antimony halides has not been defined. Synergism of halogenated compounds and free radical-generating compounds (e.g., peroxides) appears to be an artifact attributable to melt viscosity depression and dripping. Nitrogen phosphorus synergism is significant in the fire retardation of cellulose, but is dependent on the structure of the nitrogen compound — possibly involving catalysis of phosphorylation by the nitrogen compound. Other reports of synergism have dubious significance, primarily because the effects are not well defined in terms of quantitative relationships between fire retardant concentration and response.

CHAPTER 5

ELASTOMERS

5.1 Introduction

Conventional elastomers consist of flexible linear chainlike molecules cross-linked (cured) to form a three-dimensional network. Newer thermoplastic elastomers are heterogeneous (generally two-phase) systems in which glassy or crystalline domains, interspersed in the rubber matrix, act as multifunctional crosslink points.

The terms elastomer and rubber will be used interchangeably in this report. Elastomers are distinguished from other materials in being able to sustain very large (up to 700-1,000 percent) reversible deformations. They are essential in all applications when this property is required.

Most rubbers are compounded, i.e., they contain additives. These additives may be part of the curing system or may be added as reinforcement or for other special effects. In practical applications, elastomers are used rarely by themselves and are usually employed in combination with other materials, often with fibers and metals.

Elastomers that account for the bulk of rubbers used today are shown in Table 7, together with their approximate consumption in the United States in 1972. Although these statistics are not completely up-to-date, they illustrate the general scope.

The chemistry, physics, and technology of rubbers are described in several texts (Kennedy and Tornquist, 1968; Bateman, 1963; Treloar, 1958; Morton, 1972; Stern, 1967; Winspear, 1972; and Whitby et al., 1954).

Most organic elastomers burn easily when not fire retarded. Today, no elastomer has the desired combination of low flammability, low smoke emission, good mechanical properties, and reasonable cost (Einhorn, 1971; Fabris and Sommer, 1973). Prime areas of concern are coated fabrics, wire and cable coatings, hoses, and foamed elastomers.

5.2 Fire Safety Aspects of Elastomers

The fire retardation of natural and synthetic rubbers has recently been surveyed in detail by Fabris and Sommers (1973). As with most organic polymeric materials, the incorporation of halogens, either in an additive or as an integral part of the molecule, decrease the flammability of elastomers. This is illustrated by polychloroprene, chlorinated polyolefins, epichlorohydrin rubbers, the various fluoro and chlorofluoro elastomers, halogen-containing polyurethanes, and various compositions in which halogenated additives are used. All these materials have

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TABLE 7
CONSUMPTION OF NEW RUBBERS IN THE UNITED STATES 1972

Type	Amount Sold MM lbs
Styrene-Butadiene	3,189
Natural	1,411
Polybutadiene	682
Polychloroprene	273
Butyl (1)	268
Polyisoprene	250
Ethylene-Propylene-Diene	141
Nitrile (2)	141
Chlorosulfonated Polyethylene	50
Polysulfide	50
Silicone	50
Fluoroelastomers	50
Polyacrylates	50
Polybutene	50
Polyisobutylene	50
Epichlorohydrin	< 50

(1) Includes Chlorobutyl

(2) Includes Nitrile/PVC

Source: Pariser, et al (1974)

deficiencies in their fire safety characteristics (Gross, et al., 1969); they give off smoke and hydrogen halides on combustion and/or exposure to an intense fire environment. In addition, some rubbers (particularly fluorinated materials) have the potential for generating other specific toxic combustion products.

As with other organic polymers, phosphorus compounds also are used to decrease flammability. In the elastomer area, their use is generally limited to plasticized poly(vinyl chloride) and polyurethanes. In the latter category, phosphorus compounds generally form an integral part of the polymer. Materials, fire retarded with phosphorus, have somewhat lower flame propagation and are more difficult to ignite by small ignition sources, but show little improvement when exposed to intense fire situations (Trexler, 1973).

A principal method of improving the fire resistance of many polymeric materials is to promote char formation by structural modifications or by the use of additives (Vojvodich, 1969). Char production reduces the amount of fuel fed to the flame and thus reduces flammability and smoke formation. Highly cyclic and/or aromatic rigid chain structures are used to induce char formation. In contrast, linear flexible molecules are required to form an elastomer with the right mechanical

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properties, but structures with these features do not usually form char.

The third approach to reducing flammability (and smoke) consists of replacing all or part of the carbon in the polymer structure with inorganic elements (Laur, 1970). A prime example of this approach is the family of silicone elastomers (Laur, 1970; Hooker Chemical Corp., 1970; Pepe, 1970) and the still developmental phosphonitrilic elastomers (Hagnauer and Schneider, 1972).

A fourth approach is to incorporate large amounts of inorganic fillers, which reduce the fuel value of a composition even if the fillers have no specific fire retardant properties. Fortunately, most elastomers can tolerate or even require a substantial amount (≥ 50 percent) of particulate inorganic filler (Trexler, 1973). Alumina trihydrate is particularly effective because of the endothermic release of water.

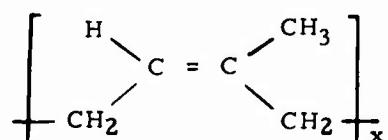
5.3 Specific Elastomers

Fire safety aspects of elastomers are largely determined by their chemical structure. From this point of view they may conveniently be assigned to several distinct groups described below.

5.3.1 Hydrocarbon-based Elastomers

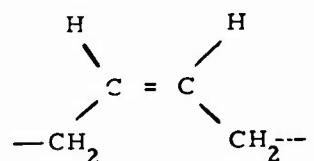
This group includes natural rubber, synthetic cis-polyisoprene, polybutadiene, styrene-butadiene rubber, butyl rubber, and ethylene-propylene rubber as its main constituents (Kennedy and Tornquist, 1968; Bateman, 1968; Morton, 1972; Stern, 1967; Winspear, 1972; and Whitby, et al., 1954).

Natural rubber is obtained in latex (emulsion) form from the rubber tree *Hevea brasiliensis*. It consists essentially of a cis-1,4-polyisoprene:



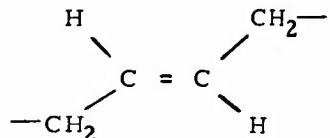
Synthetic polyisoprene is obtained through the anionic polymerization of isoprene.

Polybutadiene is manufactured in various grades containing different ratios of cis-1,4-addition,

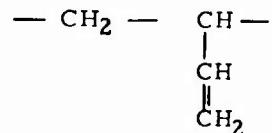


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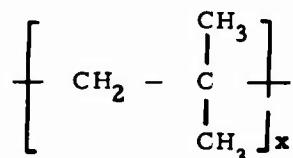
trans-1,4-addition,



and some 1,2-addition,



Styrene-butadiene rubber (SBR) is sold in the largest quantity. It is a random copolymer of styrene and butadiene, the latter occurring in the additions discussed above. The SBR used in passenger car tires (major single use) contains about 75 per cent butadiene; SBR latex paints contain about 60 percent butadiene. Thermoplastic elastomers, in the form of block copolymers of styrene and 1,4-butadiene, have also come on the market (Kraton®). Butyl rubber is polyisobutylene,



containing a small percentage of isoprene for ease of crosslinking. It is distinguished by low permeability to air. Chlorobutyl is a chlorinated derivative of butyl rubber.

Ethylene-propylene rubber (EPR) is a random copolymer of ethylene and propylene. Ethylene-propylene-diene monomer (EPDM) rubber contains a small percentage of an unsaturated molecule (the diene monomer) for ease of crosslinking.

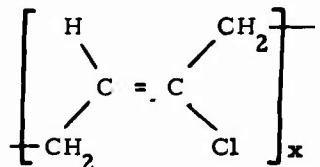
Because these rubbers are low-cost materials with good mechanical properties, they are used in large volume, but burn readily with much smoke. Fire retardant additives reduce flame spread and ease of ignition from low-energy ignition sources, but do not prevent burning in an intense fire situation. Alumina trihydrate is receiving intensive study as a filler to reduce flammability and smoke formation in these elastomers (Texas-U.S. Chemical Co., 1964; Hecker, 1968; Dalzell and Nulph, 1970; Hooker Chemical Co., 1970; Polstar, 1970).

5.3.2 Chlorine-Containing Elastomers

These elastomers include polychloroprene, chlorinated ethylene polymers and

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copolymers (chlorinated polyolefins) as well as epichlorohydrin rubbers (Morton, 1972; Stern, 1967, Winspear, 1972; and Whitby, et al., 1954). Polychloroprene



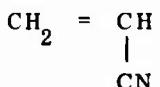
is usually crosslinked with zinc or magnesium oxide.

Polychloroprene has good mechanical properties, good oil resistance, is reasonably priced and widely used where a fire retarded elastomer is required. A wide variety of formulations of polychloroprene are available for various uses (Trexler, 1973). The material has significantly better fire retardance than the straight hydrocarbon rubber. It does, however, generate large amounts of black smoke and hydrogen chloride gas when exposed to a fully developed fire.

Chlorinated and chlorosulfonated polyolefins (Willis, et al., 1965) find relatively little usage. In their fire safety aspects they resemble polychloroprene.

5.3.3 Nitrile Rubbers

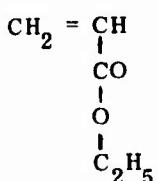
Nitrile rubbers are copolymers of butadiene and acrylonitrile.



The ratio of butadiene to acrylonitrile is similar to the ratio of butadiene to styrene in SBR. The cyanide group imparts to these elastomers some properties of the halogen-containing rubbers, except for flammability. Because of their excellent resistance to hydrocarbons (superior to that of polychloroprene), they are extensively used in gasoline hoses and fuel tanks. They also find application in adhesives. Under fire conditions, the cyanide group constitutes a potential toxicological hazard (source of hydrogen cyanide). Nitrile rubber often is used in blends with poly(vinyl chloride).

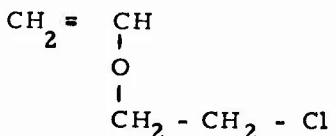
5.3.4 Polyacrylate Elastomers

A series of polyacrylate elastomers are made by polymerization of esters of acrylic acid or by copolymerization of such monomers with other monomers (Morton, 1972; Whitby, et al., 1954). A typical polyacrylate elastomer is made from ethyl acrylate,



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and 2-chloroethyl vinyl ether:

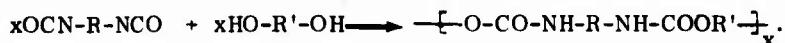


Polyacrylates can be crosslinked by reaction with various reagents such as diamines or peroxides. More commonly, however, reactive sites are introduced by copolymerizing an acrylic ester with a small proportion of a monomer containing an appropriate substitute: (Cl, —CN, —COOH).

Polyacrylate rubbers show excellent oil resistance at elevated temperatures (140°C). They are used for O-rings, gaskets, hose, oil seals, and wire insulation. These rubbers may be expected to be highly flammable.

5.3.5 Polyurethane Elastomers

Polyurethanes are polymers containing the group —NH—CO—O— (Saunders and Frisch, 1962). They are formed typically through the reaction of a diisocyanate and a glycol:



Because a variety of glycols or esters can be coupled with different diisocyanates, a large variety of linear polymers can be obtained in this way. These elastomers are crosslinked by including a controlled amount of a polyfunctional monomer (e.g., a triisocyanata or trihydric alcohol) in the reaction.

Polyurethane elastomers have outstanding mechanical properties, are moderately priced, and have unique fabrication capabilities. For these reasons they are used in a variety of rubber goods. Fire-retardant grades, generally based on bromine and/or phosphorus containing additives, are available, but they break down and burn in intense fires. Smoke generation is generally less than with hydrocarbon elastomers, but some hydrogen cyanide gas can be generated. The major use of polyurethane elastomers is in foams.

5.3.6 Polysulfide Rubbers

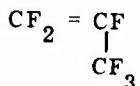
These rubbers, also known as thiokols, are polymers composed of aliphatic hydrocarbon chains connected by di-, tri-, and tetrasulfide links. (Morton, 1972; Stern, 1967; Whitby et al., 1954). Because of their outstanding resistance to hydrocarbons, they are used extensively as sealants in aircraft fuel tanks and pressurized cabins. Polysulfide rubbers are usually crosslinked by heating with zinc oxide or zinc peroxide, but other curing systems also are used. The flammability of a cured

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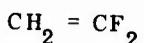
polymer may be improved by the incorporation of halogen, phosphorus, or antimony-containing compounds.

5.3.7 Fluorocarbon Elastomers

In these elastomers, hydrogen is replaced partially or wholly by fluorine (Sauers, 1970; Moran, 1959; Minnesota Mining and Manufacturing Co.; Arnold, et al., 1973). Vitons® are essentially copolymer of hexafluoropropylene,

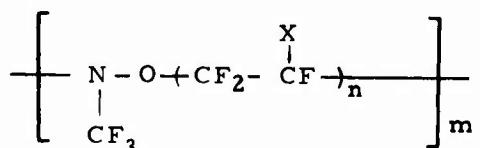


and vinylidene fluoride,



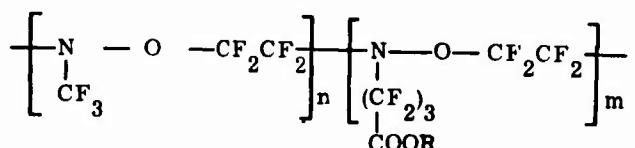
They may contain small amounts of another monomer to allow crosslinking. Fluoroelastomers, because of their high fluorine content, do not support combustion. They extinguish immediately upon withdrawal of a flame.

Specialty rubbers such as nitroso and triazine elastomers have been reported to be nonburning by the most rigid standards. Nitroso rubbers are copolymers of trifluoronitrosomethane with tetrafluoroethylene or (substituted) trifluoroethylene, represented by the following formula:



in which X = H, F, or $\text{CF}_2 - \text{COOH}$. The latter serves for crosslinking. The thermal stability of these copolymers was studied by Wright (1961). They are extremely resistant to chemical attack, but give vulcanizates with relatively poor mechanical properties.

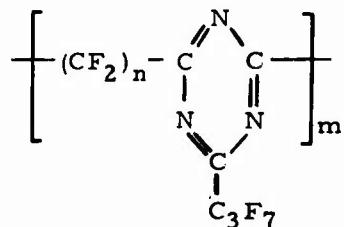
An improvement in this respect was the development of carboxynitroso rubber (Sauers, 1970; Levine, 1969 and 1971). These elastomers are made by the copolymerization of tetrafluoroethylene, trifluoronitrosomethane, and perfluoronitrosobutyric acid or its esters. Their general composition is represented by:



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where R = H or alkyn, n = 99, and m = 1. The polymers are curable with metal oxides, epoxies, salts of fluorocarboxylic and other organic acids. Even though both nitroso rubbers and carboxynitroso rubbers decompose at relatively low temperatures, the volatiles generated from the nitroso elastomers pose a significant toxic threat, particularly under confined conditions because carbonyl fluoride and other compounds are eliminated exothermically.

Triazine elastomers have been described by Graham (1969) and by Dorfmann and co-workers (1969). The materials are composed of triazine rings separated by perfluorinated polymethylene groups and carrying only perfluoroalkyl substituents:



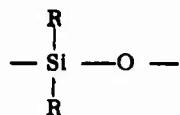
These polymers have outstanding thermal stability and retain their elastomeric character after exposure to 260 to 430°C, but are still largely experimental.

The most recent class of fluorocarbon elastomers are perfluoro ethers. A typical number of this class is a copolymer of tetrafluoroethylene with perfluoro vinyl methyl ether, $\text{CF}_2 = \text{CF} - \text{O} - \text{CF}_3$.

As a class, fluorocarbons (especially the experimental specialty rubbers) are expensive and commonly deficient in mechanical properties for many applications. They are generally difficult to ignite and not prone to propagate flames, but their products of combustion and/or pyrolysis in intense fires present potential toxicity hazards.

5.3.8 Silicone Rubbers

Silicone rubbers typically contain the repeat unit



where R is a hydrocarbon radical (Laur, 1970; Hooker Chemical Corp., 1970; Pepe, 1971). The chain backbone of these rubbers is therefore inorganic. Finely divided silica is used as a reinforcing filler to obtain useful elastomeric properties. Crosslinking is usually achieved by organic peroxides or by polyfunctional silanes.

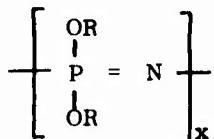
Silicone elastomers generate relatively little smoke, they are fire resistant in air, and when burned, have low fuel values (Dow Corning Corp., 1969; Compton,

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1967; Karstedt, 1970). They burn slowly and produce no flaming drip, but are relatively expensive (less so than fluorocarbon, but more so than hydrocarbon rubbers). For many applications their mechanical properties are marginal. Silicones, however, offer promising combinations of fire safety aspects, physical properties and cost.

5.3.9 Phosphonitrilic Elastomers

Phosphonitrilic elastomers represent another example of "inorganic elastomers" (Hagnauer and Schneider, 1972). The phosphorus-nitrogen backbone,



supplies the flexibility required for elastomeric properties and contributes little fuel value. The various side groups (R) affect many characteristics of the elastomers including their flammability. For example, long hydrocarbon side chains would increase their flammability while fluorocarbon side chains would not contribute to flammability but could contribute to undesirable pyrolysis products.

The phosphonitrilic materials are in early stages of development. Much needs be done to define their utility and feasibility for various applications. For example, the combustion and pyrolysis products, contributed by the phosphorus and nitrogen, need to be characterised. Phosphonitrilic elastomers are, however, one of the principal present hopes for a low smoke, low flammability elastomer.

CHAPTER 6

PLASTICS

6.1 Introduction

In this chapter, the general fire safety aspects of various types of currently available plastics and their current applications are summarized. Specific information on the properties and application of most of these materials are documented in the *Modern Plastics Encyclopedia* (1973-1974) and in the textbooks by Billmeyer (1971) and Brydson (1975). The *Polymer Handbook* (Brandrup and Immergut, 1974) and the *Handbook of Common Polymers* (Scott and Roff, 1971) also are excellent sources of data. Table 8 presents data on the U.S. sales volumes of the major plastics in 1973 and 1974.

TABLE 8
PLASTICS SALES IN THE U. S. IN 1973 AND 1974
(IN THOUSANDS OF METRIC TONS)

Material	1973	1974
Acrylic	233	243
Alkyd ^a	334	388
Cellulosics	77	76
Coumarone-indene and petroleum resins	160	160
Epoxy	102	106
Nylon	87	88
Phenolic	624	587
Polyester	468	425
Polyethylene (high density)	1,248	1,275
Polyethylene (low density)	2,691	2,769
Polypropylene	1,012	1,061
Polystyrene and styrene copolymers	2,356	2,328
Polyurethane	593	622
Poly(vinyl chloride) and other vinyl copolymers	2,151	2,180
Other vinyls	390	420
Urea and melamine	488	475
Others ^b	138	147
Total	13,152	13,350

Note: Data from *Modern Plastics*, January 1975

a. Includes captive consumption (about 50 percent)

b. Includes polyacetal, polybutylene, fluoroplastics, polycarbonate, silicones, thermoplastic polyesters, thermoplastic urethanes and others.

The term "plastics" as used here refers to rigid synthetic polymeric materials when employed either as three-dimensional solids, as films or sheets. Fibers, foams, elastomers, coatings, and natural polymers are discussed in other chapters. Plastic materials discussed in this chapter have been divided into four groups: (1)

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thermoplastic resins, (2) thermosetting resins, (3) specialty plastics, and (4) new materials under development. Within these groups, the individual plastics are covered by general types. The discussion is preceded by a consideration of general approaches that have been taken to improve the fire safety of plastics. The chapter concludes with some brief remarks concerning composites and laminates.

Table 9 presents Limiting Oxygen Index (LOI) values for several important plastics. For a brief discussion of the LOI Test and its limitations see Chapter 5, Section 4.1 Introduction.

TABLE 9
LIMITING OXYGEN INDICES OF VARIOUS PLASTICS

Plastics	LOI (% O ₂)
Polyacetal	15.0
Poly(methyl methacrylate)	17.3
Polyethylene	17.4
Polypropylene	17.5
Polystyrene	17.8
Poly(4-methylpentene)	18.0
Filter paper (cellulose)	18.2
ABS resin	18.8
Cellulose Acetate	19.0
Styrene-acrylonitrile	19.1
Poly(ethylene terephthalate)	20.0
Birch wood	20.5
Poly(vinyl fluoride)	22.6
Chlorinated Polyether (Penton [®])	23.2
Noryl [®] 731	24.3
Nylon 66	24.3
Polycarbonate	24.9
Nylon 6	26.4
Poly(phenylene oxide)	30.0
Poly(sulfone, P-1700)	30.0
Polyimides	31 - >45
Polyimide (Kapton [®] film)	36.5
Polyulfone (PES)	38.0
Poly(phenylene sulfide)	>40.0
Poly(vinyl chloride)	40.3
Poly(vinylidene fluoride)	43.7
Chlorinated PVC	45.0
Polyulfone (Astre [®])	>50.0
Poly(vinylidene chloride)	60.0
Polytetrafluoroethylene	95.0

Note: Data from Fennimore (1966); Isaacs (1970); Imhof (1973); and Stuben (1973).

6.2 Approaches To The Fire Retardation of Plastics

The following short summary of methods of fire retardation as applied to plastics should not be considered to be a comprehensive review of the subject. For a more detailed treatment the reader should consult Hindersinn and Wagner (1967), Lyons (1970), and Kuryla and Papa (1973).

Fire retardation may be achieved either by using an external coating or by incorporating fire retardants in the bulk of the material. A brief description of fire retardant coatings and a discussion of pertinent aspects of the chief fire retardant compound is presented below.

6.2.1 Fire Retardant Coatings

The use of fire retardant coatings to protect flammable substrates is one of the oldest of fire retardant methods. The coatings are of two forms, intumescent

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and nonintumescence, with the former being more useful. Intumescence coatings combine film-forming characteristics with char or ash-forming and gas-producing capabilities. The char or ash formers (generally polyhydric materials such as starch) are known as carbonifics; the gas-producing agents are called spumifics. Exposure of such coatings to flame produce a viscous carbonaceous or inorganic mass that expands into a foam by the gas generated. This thermally stable insulating char or ash protects the substrate from the thermal effects of the flame.

6.2.2 Halogen Fire Retardants

Chlorine and bromine compounds are the materials most generally employed in polymer fire retardant applications. These materials have been used successfully to retard the burning of a wide variety of synthetic and naturally occurring polymers including wood, cellulose and cellulose derivatives, wool, polyethylene, polypropylene, other synthetic polyolefins, polyesters, polyurethanes, polyamides, and many other polymers. Their wide applicability has so increased their utilization that halogen compounds, usually used together with antimony or phosphorus, now (1974) compose a market of more than 100 million pounds per year.

Halogen fire retardants may be divided into additives and chemically reactive monomers. The additives are usually combined with the polymer during processing and do not react chemically with it. Reactive monomers are chemically reacted into the polymer structure at some processing stage. Common halogenated fire retardants of both types are listed in Table 10.

TABLE 10
COMMON HALOGEN CONTAINING FIRE RETARDANTS

<u>Additives</u>	<u>Reactive Monomers</u>
chlorinated paraffins	chlorendic acid
chlorinated biphenyls*	tetrachlorophthalic acid
octabromodiphenyl ether	tetrabromophthalic acid
hexachlorocyclopentadiene derivatives	bis(2-hydroxyethylamino)-
tris(2,3-dibromopropyl) phosphate	octachlorobiphenyl

*No longer used because of environmental and health hazards.

Although halogen fire retardants are capable of imparting a considerable degree of fire retardance to polymers by themselves, their efficiency can often be increased considerably by the simultaneous use of selected compounds of boron, phosphorus and Group VA metals, especially antimony. These compounds are commonly referred to as halogen synergists (but see Section 4.7.4) because of their apparent tendency to increase fire retardant efficiency out of proportion to the

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amount of the material generally used. Antimony oxide and various phosphate esters are the most widely used synergists. They are added mainly to poly(vinyl chloride) compositions, although they also find considerable utility in a wide variety of fire retardant compositions including halogenated-unsaturated polyester resins and intumescent coatings.

6.2.3 Phosphorus

Inorganic and organic phosphorus compounds also have been found to be effective fire retardants in many polymers and are used almost as extensively as halogens in such applications. Although both reactive and nonreactive phosphorus fire retardants are commercially available, the additive types have attained the greatest utility.

Phosphorus compounds have found their chief use in highly oxygenated polymers such as cellulose. Their largest single commercial application, however, is as fire retardant plasticizers in PVC where they are used to prepare clear flexible compositions without the loss of fire retardance associated with the common plasticizers, such as dioctylphthalate. The market for the phosphorus compounds is estimated to amount to 43,000 metric tons in 1974, and about 90 percent of this volume finds application in PVC (Anon., 1974). Reactive phosphorus fire retardants are used most extensively in polyurethane foams where they have been found to be especially effective in reducing flammability by a char-forming condensed-phase mechanism.

Combinations of a phosphorus compound with a halogen-containing fire retardant have been reported to yield synergistic effects in many polymer compositions. For example, phosphorus esters prepared from halogen-containing alcohols are some of the most widely used fire retardants because of their high fire retardant efficiency. However, evidence for true phosphorus halogen synergism is not well established at present (Hindersinn and Witschard, 1975). Some phosphorus fire retardant additives are:

- Tricresyl phosphate
- Tris(2,3-dibromopropyl) phosphate
- Triphenyl phosphate
- Trioctyl phosphate
- Ammonium phosphate
- Tris(2,3-dichloropropyl) phosphate
- Poly- β -chloroethyl triphosphonate mixture

Fire-retardant phosphorus reactive monomers are:

- Tetrakis(hydroxymethyl)phosphonium chloride (THPC)
- Diethyl N,N-bis(2-hydroxyethyl)aminomethyl phosphonate
- Hydroxyalkyl esters of phosphorus acids

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6.2.4 Other Fire Retardants

Various boron compounds have found some use as fire retardants, especially in cellulose. They have been added to other polymers as low cost substitutes for antimony oxide where they show a degree of activity as halogen synergists. They are especially useful in suppressing the afterglow that often results from the use of halogen-antimony combinations in cellulose and other oxygen containing polymers. The most commonly used boron fire retardant is zinc borate.

Hydrated aluminum oxide has become increasingly important in recent years as a fire retardant additive. It has been used extensively in some fire retardant polyester compositions and in elastomers used in such applications as carpets and rugs because of its low cost. Sales of alumina trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) have increased rapidly in the past few years; for 1974, sales are estimated at about 86,000 metric tons (Anon, 1974).

6.3 Thermoplastic Resins

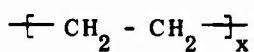
Included under this heading are polyolefins, styrene polymers, poly(vinyl chloride), acrylics, acetals, cellulosics, polyamides, and thermoplastic polyesters. The "big three" (polyolefins, poly(vinyl chloride), and styrene polymers) represent over 70 percent of the total plastics production.

Within each of these classes there are a number of specific types. For example, the styrene polymers include polystyrene, styrene/acrylonitrile copolymer, polystyrene-rubber blends (high-impact polystyrene), ABS resins (acrylonitrile-butadiene-styrene), and other styrene copolymers, graft polymers, and blends. Even for one specific type there are many variations in polymer composition, additives, fillers, molecular weight, molecular structure, etc. These variations not only affect physical properties, but also can have an effect on fire safety characteristics.

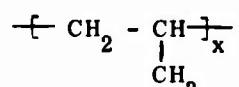
As their name denotes, thermoplastics soften when heated. In a fire, such materials can soften enough to flow under their own weight and drip or run. The extent of dripping or running depends on thermal environment, polymer structure, molecular weight, presence of additives or fillers, etc. Dripping or running of molten polymer can increase or decrease the fire hazard depending on the particular fire situation (i.e., With small ignition sources, removal of heat and flame by the dripping away of a burning polymer can protect the rest of the material from spreading of the flame. In other situations, the flaming molten polymer might flow and ignite other materials.)

6.3.1 Polyolefins

The major polyolefin plastics are low density polyethylene, high density polyethylene, and polypropylene:



Polyethylene



Polypropylene

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Polyethylene is crystalline and its density is directly related to its degree of crystallinity. Polypropylene is isotactic and crystalline. Smaller volume materials are polybutene, poly(4-methylpentene), poly(ethylene-co-vinyl acetate), other copolymers, and blends. Polyolefins differ mainly in modulus and melting or softening point, which are functions of the type of the olefin, chain branching, as well as type and amount of comonomer. The latter two properties strongly affect the degree of crystallinity.

Polyolefin production represents over 35 per cent of the total plastics production (see Table 8). Film accounts for 30 percent of polyolefin production and 25 percent is used in molding. The remainder is used in pipe and other extruded products, wire and cable coatings, general coatings, and fibers.

Combustion of polyolefins has been extensively reviewed by Cullis (1971). Chemically, polyolefin foams are very similar to paraffin wax and they burn in somewhat the same way. They ignite easily, burn with a smoky flame, and melt as they burn. Polyolefins produce less smoke than polystyrene, and the degree of melting and dripping can be enhanced or decreased by choice of molecular weight, crosslinking, fillers, additives, etc.

The mechanism of burning of polyolefins is similar to that for most solid materials. The polymer is degraded to volatile fragments by the thermal environment. The fragments burn in the gas phase. Since polyolefins generally degrade by random chain scission rather than "unzipping" (depolymerization), volatile fragments cover the range from small gaseous hydrocarbons to large condensable fragments. These large fragments generally do not burn as cleanly as the small molecules and produce smoke.

The products of combustion of polyolefins depend on combustion of the polymer and the conditions of burning. Generally, the combustion products are those expected from burning hydrocarbons. The major toxic material is carbon monoxide (Ball, 1973). Additives and fillers can, of course, contribute to formation of additional products of combustion.

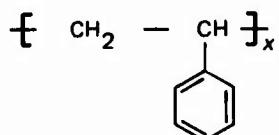
Considerable effort has been devoted to decreasing the flammability of polyolefins. The use of additive systems based on combinations of halogen compounds and antimony oxide has been the most effective (Schwarz, 1973; Howarth, et al., 1973). Numerous formulations are available that greatly improve resistance to ignition in low thermal energy environments. Flame spread rates also can be reduced. All of these fire retardant compositions, however, can burn readily in a fully developed fire, contributing to the fuel load and producing very hot fires.

In their current major applications polyolefins present little fire hazard, but increasingly larger amounts are being used and many diverse applications are being developed. This is accentuated by the increasing use of polyolefin-based structural foams and moldings as well as their applications in relatively large items such as pallets, furniture, and bins. Therefore, danger exists that excessive fuel loads and paths for rapid flame spread may be created in the future.

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6.3.2 Styrene Polymers

Polystyrene (Guenin, 1973) is a simple amorphous polymer with the formula:



Styrene polymers include polystyrene, impact polystyrene, ABS resins, and SAN. The latter is a styrene-acrylonitrile copolymer, which generally contains about 72 percent styrene. Impact-resistant polystyrene and ABS resins are two-phase systems consisting of inclusions of rubber in a continuous amorphous matrix. In ABS resins, the matrix is a SAN copolymer and rubber is a styrene-butadiene copolymer grafted to the matrix polymer (Saxe, 1973). The ABS resins are true engineering plastics and have better temperature and solvent resistance than the impacted styrenes. Styrene is also a component in styrene-butadiene rubber and large quantities are used as foam.

Styrene polymers represent about 18 percent of the total plastics production (see Table 8). Polystyrene products derive their wide use and large volume from the combination of good overall physical properties, low material cost, and low fabrication cost. Approximately 50 percent of styrene-based polymers go into molding material, 20 percent into extrusion applications, and 10 percent into foam production. The larger volume end uses are: packaging houseware, toys, appliances, and pipe.

Styrene polymers burn readily with the evolution of dense smoke. Depending on composition, molecular weight and conditions of burning, some materials drip flaming molten polymer. Fire hazard can be reduced by the use of additives and variations in composition that decrease ease of ignition and reduce the rate of flame spread under conditions involving relatively small ignition sources and/or low energy environments. In intense fires, even the best of these compositions burn rapidly. Pound for pound styrene polymers represent about twice the fuel load of cellulose. Foam products, on a volume basis, have relatively low fuel values, but can have high burning rates.

In the major current applications, styrene plastics present little fire hazard. However, with the increasing amount and diverse uses of polystyrene foam (see 7.3.3), in addition to the proliferation of large thermoformed items potential hazards arise when relatively large amounts of polymer are stored and when large surface areas are exposed. The hazard is enhanced by the high burning rate of polystyrene and by the high temperature and dense smoke generated in polystyrene fires.

The mechanism of combustion of styrene products is reasonably well

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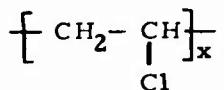
understood. The ignition source, thermal environment, and heat of combustion of the polymer supply the energy required for degradation of the polymer to monomer and polymer fragments. The fragments volatilize and burn in the gas phase. Thermogravimetric analysis shows that the polymer volatilizes rapidly at 300°C and is essentially completely volatilized at 450°C. SAN and ABS behave in a similar manner although the pyrolysis products are somewhat more complex because of the presence of acrylonitrile and/or butadiene.

The products of combustion of styrene-based polymers and physiological effects of these products have only recently begun to receive detailed attention. As with all such materials, combustion products depend on the condition of burning as well as on the structure and composition of the polymer and the additives that may be present. Few quantitative data are yet available.

An extensive array of additives has been tried to reduce the flammability of styrene-based products (Lindemann, 1973; Howarth, 1973). The majority of these additives are halogen compounds and usually incorporate a synergist such as antimony oxide. Some contain phosphorus with or without halogen. The systems are considered to function by disrupting the free radical chain process of combustion in the gas phase. Other additives are based on a peroxide or on other free radical precursors. These are believed to function by increasing the depolymerization rate and promoting dripping of molten polymer, thus removing heat and flame from the burning sample. Their use has been emphasized in styrene-based foams. Use of additives intended to blanket the burning polymer and limit access of oxygen has not proved very successful. Attempts to reduce the rate of fuel production stabilization or promotion of char have not been equally successful.

6.3.3 Polyvinyl Chloride

Vinyl chloride is an inexpensive monomer that can be polymerized by a variety of free radical initiators to yield a high-molecular-weight polymer with the general structure:



Because of its low cost and useful properties, PVC is one of the largest volume commercial thermoplastics. In 1974, more than two million metric tons were produced for a wide variety of applications. The physical properties of PVC compositions can be varied widely from rigid plastics to flexible elastomers depending upon the compounding ingredients (plasticizers) used in the formulation. Some of the largest volume applications are in flooring film and sheeting, furniture, electrical wire and cable insulation, and pipe.

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The fire retardation of PVC has been reviewed by O'Mara et al., (1973). PVC itself does not burn under most normal conditions; however, it generally is compounded with significant and often large amounts of plasticizers or processing aids, many of which are flammable (particularly the widely used phthalate, sebacate, and adipate esters, and various low molecular weight adipate polyesters). The use of such plasticizers leads to flammable PVC compositions.

When exposed to a flame or to excessive heat, PVC emits hydrogen chloride at relatively low temperatures in a highly endothermic process. This emission together with the fact that the polymer contains more than 50 percent chlorine by weight accounts for low flammability of the uncompounded polymer. Depending upon the amount or type of compounding ingredients used during fabrication, decomposition products may include benzene, hydrocarbons, char and other fragments.

The methods used to render PVC compounds fire retardant are as varied as the materials employed in the formulations, but are exclusively of the additive variety. The most commonly used additive is antimony oxide because it acts as a synergist with the chlorine contained in the polymer. Because of its incompatibility with the polymer, antimony oxide renders PVC compositions opaque, but, despite this disadvantage, about 80 percent of the antimony oxide consumed in the plastics industry is used in fire-retardant PVC compositions. As little as 2 parts of antimony trioxide per 100 parts of resin (phr) give excellent fire retardance to compositions containing up to 50 phr of primary plasticizers such as dioctyl phthalate. Up to 5 phr of antimony oxide are added ordinarily.

Chlorinated or phosphorus containing plasticizers also are used in large quantities to reduce the flammability of plasticized compositions. Among these, phosphates and chlorinated paraffins are used most widely.

Phosphates, particularly tricresyl phosphate, cresyl diphenyl phosphate, and 2-ethylhexyl diphenyl phosphate, have traditionally been added to PVC as plasticizers. They also enhance fire retardance and achieve excellent flame-out times. They are usually blended with other plasticizers to lower cost or to produce the desired physical properties. Their fire retarding effect is probably related to their moderate, but not excessive ease of thermal decomposition and propensity to generate acidic products that promote charring. Phosphate plasticizers, however, can at times interact with antimony oxide to change their decomposition mechanism thus destroying the fire retardance of both. In contrast to antimony oxide, phosphates may be used in clear film.

Other widely used fire retardant PVC plasticizers are chlorinated paraffins. These inexpensive materials contain about 40 to 60 percent chlorine and are often used in combination with phosphate plasticizers to reduce cost and to obtain special combinations of properties. They can also be combined with antimony oxide.

Halogenated hydrocarbons, such as chlorinated polyphenyls, also have been used, but their applications have recently been curtailed due to the discovery of

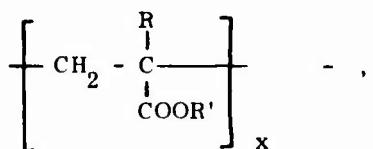
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their adverse effect on the biosphere. More complex phosphonates and chlorinated phthalates, helpful in other resin systems, are little used in PVC because of their high cost, poor compatibility, or poor performance.

Other fire retardant additives, used much less extensively than antimony oxide because of their lower efficiency, are barium metaborate, zinc borate, zinc antimony polyalkylphosphate, and zinc boron polyalkylphosphate. Hydrated zinc borates are thought to dehydrate under fire conditions to zinc chloride, boric acid, and zinc oxychloride, all of which have been used to some degree to modify the flammability characteristics of PVC. Two more expensive additives are hydrated stannic oxide and ferrocene. They are reported to generate less smoke under standard test conditions (Brighton, 1971).

6.3.4 Acrylics

Acrylics are polymers formed from acrylic ($R=H$) or methacrylic ($R = CH_3$) esters according to the formula:



where R' represents an alkyl radical.

The major plastic in this group is essentially a homopolymer of methyl methacrylate (R and $R' = CH_3$), a crystal clear material that softens at about $100^\circ C$. Various other acrylic polymers and copolymers are used in lacquer, enamel, and latex coatings. Acrylic plastics and elastomers should not be confused with acrylic fibers, which are based on acrylonitrile.

Approximately half of the 240,000 metric tons of acrylic plastics sold in 1974 were used in the form of cast sheet; major applications were used for glazing and signs. Properties that account for most uses of acrylic plastics are clarity, light and weather stability, ease of fabrication, moderate cost, and rigidity (Sawyer, 1974).

Poly(methyl methacrylate) (PMMA) ignites readily and softens as it burns. Burning rate, fuel load, and smoke production are less than for polystyrene (Hilado, 1969). In burning, PMMA undergoes pyrolysis from the heat of the ignition source, the heat of combustion, or other environmental energy (Conley and Malloy, 1970). The volatile products of pyrolysis then burn in the gas phase. Heat from combustion causes additional pyrolysis and consequent continued burning. PMMA is comparable in its flammability to the polyolefins. Its depolymerization energy (~ 14 kcal) is low compared with that of polystyrene or polyethylene (~ 20 kcal). Consequently, the pyrolysate contains much monomer and few high molecular weight products. Depolymerization by "unzipping" rather than chain scission causes

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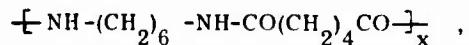
PMMA to drip less during burning than polystyrene or the polyolefins (Conley and Malloy, 1970). Unzipping, along with the presence of oxygen in the ester group, probably accounts for PMMA's lower smoke formation per unit weight in comparison with that of hydrocarbon polymers under most burning conditions. Reduced smoke formation probably also contributes to its experimentally established lower rate of burning because the less luminous flame feeds back less radiant energy to cause further pyrolysis.

Halogen and antimony compounds have been used to reduce burning rates and ease of ignition of PMMA, but less effort has been devoted to the fire retardation of PMMA than to that of other polymers (Howarth, 1973). This lack of effort is due partly to the realization that it is difficult to inhibit the "unzipping" depolymerization mechanism so characteristic of this polymer. In addition, excellent transparency and aging characteristics are prime properties of most applications of PMMA and fire retarding additives usually detract from one or both of these properties.

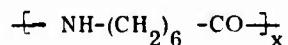
When used as glazing, particularly in relatively large areas, the potential fire hazard should be carefully analyzed. The possible contribution of acrylic glazing to the tragic Summerland fire on the Isle of Man is under investigation (Anon, 1973).

6.3.5 Nylons

The major nylon plastics are nylon 66,



and nylon 6,



Other molecular structures such as nylon 610, 612, nylon 11, and nylon 12 with different chain lengths between the amide groups are used for special purposes. Nylon polymers owe their wide application as engineering plastics to their strength, toughness, and solvent resistance.

Of the 88,000 metric tons produced in 1974, the largest single application, 25 percent, was in automotive parts. Electrical applications accounted for 12 percent, 9 percent was employed as film, and the remainder was distributed among a variety of extrusion and molding applications.

Nylon moldings are often described as "self-extinguishing," due largely to their tendency to drip when ignited (dripping removes the flame front and hot polymer from the burning piece). If dripping is prevented, nylons burn with a smoky flame. Nylons pyrolyze to a complex mixture of hydrocarbons, cyclic ketones, esters, and nitriles with some carbonization (Conley and Gaudiana, 1970).

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Volatiles burn to a variety of products depending on conditions.

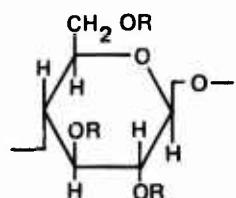
Fire retarding formulations are generally based on phosphorus-containing, or halogen-containing additives, with or without the addition of antimony; iron oxides and hydrated alumina have also been used, (Howarth, 1973; Pearce, 1975). The addition of drip promoters, such as thiourea, has been proposed. None of these systems prevents burning in a fully developed fire.

Many molding and extrusion compositions contain glass fibers or particulate mineral fillers (as much as 40 percent by weight) to enhance certain engineering properties. Such filled materials can burn more readily than the unfilled counterparts because the fillers tend to reduce dripping. Highly filled materials, however, have lower fuel value.

Currently nylons are used in relatively small items and have not, in themselves, posed serious fire safety problems. However, since larger products (such as: gas tanks, large castings, automotive body parts, other structural applications, etc.) are being considered, more attention needs to be given to the analysis of the fire hazards that might be introduced.

6.3.6 Cellulosics

Regenerated cellulose and cellulose acetate are widely used as fibers. Cellulose derivatives that are useful as plastics include regenerated cellulose, organic and inorganic esters of cellulose, and cellulose ethers. The basic building block is the substituted glucose unit:



When R= H, the structure shown depicts that for the basic cellulose monomer. The formulae for the various derivatives are obtained by replacing R as follows:

<u>Derivative</u>	<u>R</u>
Cellulose nitrate	-NO ₂
Cellulose triacetate	-COCH ₃
Cellulose propionate	-COC ₂ H ₅
Cellulose butyrate	-COC ₃ H ₇
Ethylcellulose	-C ₂ H ₅

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Regenerated cellulose (viscose) film is called cellophane. If cellophane is to be used as a moisture barrier, a very thin film of wax, nitrocellulose, poly(vinylidene chloride), or other material is applied as a coating.

Cellulose nitrate plasticized with camphor (celluloid), the first thermoplastic, was introduced in 1870, but today it accounts for only a few percent of the cellulosics market. The current major use for cellulose nitrate is in coatings.

Cellulose acetate (plasticized) is a tough, clear injection moldable plastic with good electrical properties, but it has a low softening point and high water adsorption. The higher esters, propionate and butyrate, have lower water adsorption and process easily. Because they are hard, tough, strong, and transparent, they are used in film and sheet form, in injection moldings, and in the extrusion.

Ethyl cellulose is the most widely used cellulose ether. It finds application in molding, extrusion, and sheet fabrication. It is transparent and tough even at low temperatures. Typical manufactured items are flashlight casings and electrical appliance parts. The market for cellulose esters and ethers in 1974 was 76,000 metric tons. The cellophane market was considerably larger.

The basic flammability characteristics of regenerated cellulose are comparable to those of cotton. In film form (cellophane), the flammability characteristics are somewhat dependent on the coating, if any. A poly(vinylidene chloride) coating would decrease flammability since hydrogen chloride from the pyrolysis of the coating would promote charring of the cellulose. Nitrocellulose coating on the other hand could increase flammability. Cellulose has about one half the fuel value of hydrocarbon plastics.

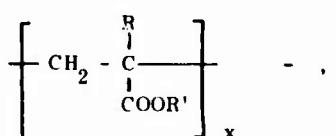
Cellulose nitrate ignites readily and burns vigorously, generating nitric oxide gases. It presents the greatest fire hazard of all plastic materials, and thus, the use of nitrocellulose lacquers in some applications could be extremely hazardous from the point of view of fire spread. Temperatures as low as 150°C can initiate decomposition and ignition. However, it is possible by proper formulation to modify its flame spread rate.

Organic cellulose esters and ethers melt and drip as they burn and give off a yellow sooty smoke. Halogen and phosphorus-containing plasticizers have been used to produce fire retardant grades, but they still burn readily in a fully developed fire (Howarth, 1973).

Essentially no information is available to the Committee on the toxicity aspects of pyrolysis and combustion products of cellulose plastics.

6.3.7 Polyacetals

The commercial polyacetals are formaldehyde polymers and copolymers terminated (capped) with esters or other groups for stabilization. The simplest polyacetal is polyoxymethylene (polyformaldehyde):



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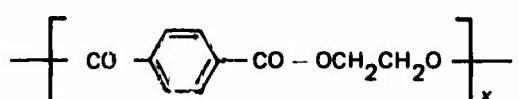
Polyacetals are widely used for their mechanical characteristics; they are tough, solvent resistant, have low friction coefficients, and can be fabricated easily by injection molding. Major applications are automotive parts, appliances, and plumbing fixtures.

Formaldehyde polymers and copolymers are characterized by low oxygen requirement for combustion (low LOI), very low smoke, and low fuel value. These properties result from their unique chemical structure. Formaldehyde polymers have an alternating carbon-oxygen backbone and pyrolyze to monomer at relatively low temperatures (230°C) (Conley and Gaudiana, 1970). The evolved formaldehyde burns with a clear blue flame accompanied by some polymer melting and dripping, depending on molecular weight, fillers, geometry, etc. Since polyformaldehyde has no carbon-carbon chains, it burns without smoke even at low oxygen levels, and the products of combustion are water, carbon dioxide, and some carbon monoxide. The carbon in polyformaldehyde is already partially oxidized (the polymer contains over 50 percent oxygen) and, thus has a relatively low fuel value. The heat of combustion is comparable to that for cellulose and about half that for hydrocarbon polymers.

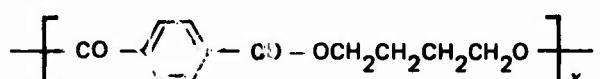
Little success has been achieved in fire retarding polyacetals because of the nature of their pyrolysis, which resembles that of PMMA. On the other hand, many of these polymers are used in relatively small parts where they do not present major fire hazards.

6.3.8 Polyesters

The polyesters included here are linear thermoplastic poly(ethylene terephthalate) (PET):



and poly(butylene terephthalate) (PBT):



and their modifications. PET, chemically identical with polyester fibers and Mylar® film, never developed a large market as a plastic due to difficulties in injection molding. However, PBT overcame these limitations and is a rapidly growing engineering thermoplastic. Usage depends on toughness, rigidity, solvent resistance, electrical properties, and general good durability. Most compositions are reinforced with glass fibers. The current major applications are in small automotive parts and in the electrical/electronic industry (McDonagh, 1972; Borman and Kramer, 1974).

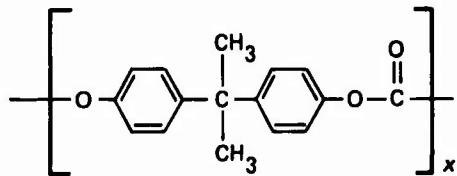
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These polymers burn with a smoky flame accompanied by melting, dripping and little char formation. A number of fire retarded grades are available and many more are reported in the literature (Shalaby and Pearce, 1974). These grades are generally prepared by incorporating halogen-containing materials as part of the polymer molecules or as additives. Metal oxide synergists are frequently included. These fire retarded systems are resistant to small ignition sources in low heat flux environments, but can still burn readily in fully developed fires.

As with other engineering thermoplastics, many end uses are in small parts that may not constitute a significant fire safety hazard in themselves. Care must be exercised in electrical and electronic applications to avoid possible ignition from electrical sources.

6.3.9 Polycarbonates

Polycarbonates are a special class of polyesters derived from bisphenols and phosgene. The commercial products are based on bisphenol-A:



Some contain fibrous or particulate fillers. Polycarbonates are extremely tough and have good creep resistance. Over 40 percent of production is used in appliances and electronic devices; other uses are in transportation, sports equipment, signs and glazing.

Commercial unmodified polycarbonates are significantly less flammable than unmodified styrene, olefin, or acrylic polymers. Some char is produced during pyrolysis or burning. They extinguish during simple horizontal burning tests and have an oxygen index significantly above those of all the previously discussed unmodified thermoplastics (see Table 9) (Hilado, 1969). Their fire resistance has been further improved by the use of halogenated bisphenols in the preparation of the polymer or by the use of halogen-containing additives with or without antimony oxide (Howarth, 1973). Polycarbonates will burn under high thermal fluxes. Little information is available on the toxicity of their combustion products. Those containing halogens would be expected to evolve some hydrogen halide.

6.3.10 High Nitrile-Containing Polymers

A number of copolymers containing high percentages of acrylonitrile or methacrylonitrile have recently been developed specifically for packaging carbonated beverages and food items. The common characteristics of these materials are

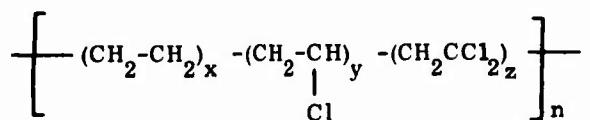
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their low transmission of oxygen, carbon dioxide, and water.

No details are available on the flammability of these polymers. They have been reported to be disposable in normal waste channels without adversely affecting incineration operations or causing changes in effluent composition (Idol and Moncure, 1973). From their composition, they would be expected to burn with smoky flames. The products of combustion would vary with the composition and burning conditions, but all are likely to evolve some hydrogen cyanide.

6.3.11 Chlorinated and Chlorosulfonated Polyethylene

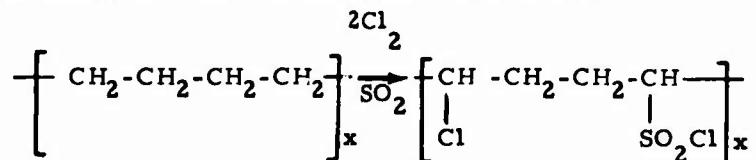
Polyethylene can be chlorinated in the presence of light or free radical catalysts to give a chlorinated polymer of the following general structure (Canterino, 1967):



The chlorine content, and therefore the properties of the product, can vary considerably depending upon the extent of chlorination and reaction conditions. Flammability decreases directly with the chlorine content. Various compositions containing 25 to 40 percent chlorine by weight are reported to extinguish under ASTM D-635 conditions. Compositions containing as much as 67 percent chlorine have been prepared. As with chlorinated polymers in general, antimony oxide enhances the efficiency of the halogen and, within limits, reduces the amount of chlorine required to yield the desired fire retardant properties.

As the chlorine content of chlorinated polyethylene increases, it approaches a mixture of the chemical structures associated with poly(vinyl chloride) and poly(vinylidene chloride); therefore, its flammability characteristics resemble those of these two common chlorinated polymers. Hydrogen chloride is a major combustion product. Commercial products contain 40 to 45 percent chlorine and are used extensively as impact modifiers for poly(vinyl chloride) and poly(vinyl acetate) compositions, the major applications being in vinyl tile flooring.

Polyethylene can be chlorosulfonated by methods similar to those used in the chlorination already described. The reaction is represented by:



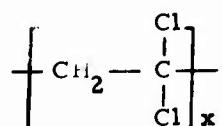
As in chlorination, the properties of the composition can be varied widely depending upon the extent of chlorosulfonation and reaction conditions.

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As expected, flammability of the polyethylene is reduced as the chlorosulfonyl chloride content is increased. Chlorosulfonated polyethylene, sold commercially under the trade name Hypalon®, has an LOI of 27 as compared to 18 for unmodified polyethylene. Its flammability has received little study to date; presumably hydrogen chloride and sulfur oxides are major products of combustion.

6.3.12 Vinylidene Chloride Polymers

Poly(vinylidene chloride):



possesses an unusually low permeability to gases and vapors. This property can be exploited best in the form of films or coatings and it is in these forms that vinylidene polymers find their greatest utility. Poly(vinylidene chloride) homopolymers suffer from poor thermal stability, but this problem can be overcome by copolymerization with other monomers. Commercialization of vinylidene polymers by the Dow Company began in 1939 under the trade name Saran (Wessling and Richards, 1971).

The homopolymer (Saran A), although it has valuable properties, was not produced commercially because of difficulties in fabrication related to its poor thermal stability. A great many copolymers were prepared, but only vinylidene chloride-alkyl acrylate copolymers (Saran C), and vinylidene chloride-acrylonitrile copolymers (Saran F) have stood the test of time. Many of the materials identified in the literature as poly(vinylidene chloride) (or PVDC) were actually copolymers of unknown composition.

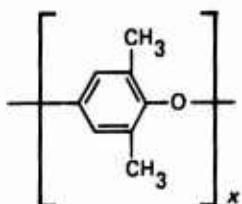
Most common test methods indicate that vinylidene chloride polymers have a low degree of flammability. They have a LOI of 60, which is higher than that of most thermoplastics produced in larger volume. This resistance to combustion is not only a function of their high chlorine content, but also is related to their tendency to dehydrochlorinate into a carbonaceous char highly resistant to combustion. Large volume of hydrogen chloride are produced as a byproduct of this carbonization reaction.

Vinylidene polymers are produced in relatively small amount because of their relatively high cost. They are little used in applications where fire retardance is of prime importance.

6.3.13 Poly(aryl ethers)

PPO®, a commercially available poly(aryl ether), is prepared by the oxidative coupling of 2,6-xylenol to give:

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This material is a rigid, tough, chemically and thermally resistant thermoplastic with good electrical properties. It has been proposed for various engineering and electrical applications. Major consumption appears to be in blends with polystyrenes. These blends (trade named Noryl®) have thermal and mechanical properties and costs intermediate between ABS resins and polycarbonates. Glass-filled modifications are available. Major applications are in automotive and electrical parts.

Poly(aryl ethers) are char forming and have flammability characteristics similar to those of some of the polysulfones. Blends with polystyrene (Noryl®), reduce the dripping of polystyrene and make ignition more difficult. Fire retarded versions, based on halogenated coreactants or organophosphate additives are available. No data are available on their combustion products.

6.4 Thermosetting Resins

Thermoset polymers are distinguished from thermoplastics in that they become chemically crosslinked during final molding and curing. For most practical purposes, they can no longer be melted, reshaped or dissolved. Polymerization of thermoset resins generally is divided into two stages: in the first stage, a relatively low molecular weight prepolymer is formed which can be melted, dissolved, or molded; in the second stage, the prepolymer is crosslinked (cured) with or without the application of heat in the presence of suitable catalysts, activators or promoters, or crosslinking monomers. Sometimes an inhibitor is added to the first stage to prevent premature curing.

Thermosetting resins are produced in large quantities and are extensively used in the construction, housing, and large appliance industries where they may contribute significantly to the fire load in any particular area or product. Consequently, their fire safety characteristics are of primary concern. Because of their crosslinked nature, thermosets generally do not soften or drip when exposed to a flame as do many thermoplastic materials. Their flammability is a function of the thermal stability of the primary chemical bonds and the ease with which volatile gaseous products can be produced by pyrolytic processes to provide fuel for a self-sustaining fire. Many thermosets (e.g., the phenolic resins) produce very little flammable fuel when heated by an ignition source. They produce an insulating char that can only be oxidized at extremely high temperatures and/or high oxygen concentra-

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tions. Burning of such materials can be a slow process under many conditions since the polymer substrate is protected by the surface char. Such resins are inherently fire retardant and will pass many common laboratory tests without the need of a fire-retardant modification or additive. Their fire retardance, however, is a function of the mechanical stability of the insulating char and is limited by the resistance of elemental carbon to oxidation. Other thermosets (e.g., styrenated polyester resins) do not form chars, but pyrolyse to yield volatile combustibles, and burn readily.

6.4.1 Phenolic Resins and Molding Compounds

Phenolic resins are prepared by the condensation of phenol and formaldehyde. Depending on the catalyst, the phenol/formaldehyde ratio and the reaction conditions, two general types of first-stage phenolic resin are produced: resoles and novolaks. Resoles are used mainly as water-resistant adhesives in the plywood industry. Novolak resins are used widely in the electrical appliance and automotive parts market because their thermal stability, good electrical properties, resistance to combustion, and low costs have been major assets. The volume of phenolic resins continues to grow with more than 500,000 metric tons being sold in 1974. They are used almost exclusively in filler systems (composites).

Physical properties of phenolic resins vary widely depending upon the type, kind and amount of filler, kind of reinforcement, phenol/formaldehyde ratio, type of curing catalyst, and other formulation variables. Their chemistry is too involved to be described in detail here. More information may be found in Bydsen (1975), Billmeyer (1971), and Foy (1969).

Resoles are liquid resinous products prepared by the condensation of phenol with formaldehyde in ratios greater than 1:1 to as high as 1:3 in the presence of an alkaline catalyst. During this primary condensation step, the reaction conditions must be carefully controlled to prevent premature crosslinking or curing. The resole is normally set (or cured) by a simple thermal treatment although room-temperature cures are possible by the addition of a suitably active catalyst. Resoles are inherently unstable and must be stored and handled carefully to avoid premature setting.

If a phenol/formaldehyde ratio of one or less is used in the initial condensation with an acidic catalyst, thermally stable resinous thermoplastic polymers, commonly referred to as novolaks, can be formed. These resins can be formulated subsequently with fillers, colorants, reinforcing agents, catalysts, and additional formaldehyde (or formaldehyde generator) to form the commercially important molding compounds. The most common formaldehyde substitute used in these resins is hexamethylenetetramine, more commonly known as "hexa." This compound is an inexpensive stable solid that can be converted easily to formaldehyde by heating.

Cured phenolic resins do not ignite easily because of their high thermal stability and high charring tendency in the presence of fire and heat (Sunshine, 1973).

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Flammability of the end products can vary widely however, depending upon the amount and type of filler used the crosslink density, amount and type of reinforcement, and other less important formulation variables. The principal volatile decomposition products are methane, acetone, carbon monoxide, propanol, and propane. A variety of additives have been found to be useful in applications where a degree of fire retardance above that inherent in the polymer is required. The following fire retardant methods have been most commonly used:

1. addition of halogenated paraffins
2. addition of phosphorus compounds and halogenated phosphorus compounds
3. addition of hydrated alumina or zinc borate
4. increased crosslink density

6.4.2 Unsaturated Polyester Resins

Two classes of thermoset resins are commonly referred to as polyester resins — the alkyds and the so-called unsaturated polyester resins. Unsaturated resins are prepared by condensing a saturated dibasic alcohol plus both a saturated and an unsaturated dicarboxylic acid into a prepolymer (or first stage) resin. The prepolymer is then dissolved in a vinyl monomer, usually styrene. The cured resin is produced by free radical copolymerization of styrene monomers and unsaturated acid residues. The upper part of Figure 2 represents the unsaturated low-molecular-weight polyester prepolymer (a) and the styrene monomer (b) before curing; the lower part represents the structure resulting from the curing (i.e., crosslinking through copolymerization).

Economic considerations generally limit the unsaturated dicarboxylic acid to maleic or fumaric acid. A variety of saturated dicarboxylic acids or hydroxylic compounds may be employed to obtain a range of physical properties. Phthalic anhydride is used most widely as the saturated acid component. The resins usually are compounded with a reinforcing glass fiber or filler before curing.

Because of their versatility and low cost, unsaturated polyester resins are extensively used in large-scale applications in the construction industry, the chemical process industry, and manufacture of small boats, etc. Production and sale of unsaturated polyester resins is expected to reach 2 billion pounds in 1978 with fire retardant compositions representing only a small portion of this total. The burning characteristics of unsaturated polyesters can be modified by addition of inorganic fillers, addition of organic fire retardants, chemical modification of the acid, alcohol or unsaturated monomer component, and the chemical combination of organometallic compounds with the resin (Nametz, 1967; Roberts et al., 1964).

It is common practice to add an inert filler to polyester compositions to reinforce the cured composite, to lower its cost, and to improve its fire retardance. Glass fiber and calcium carbonate often increase the burning rate of the composition but other fillers may have some fire retarding effects. Very few fillers are being

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Uncured and Cured Polyester Resin

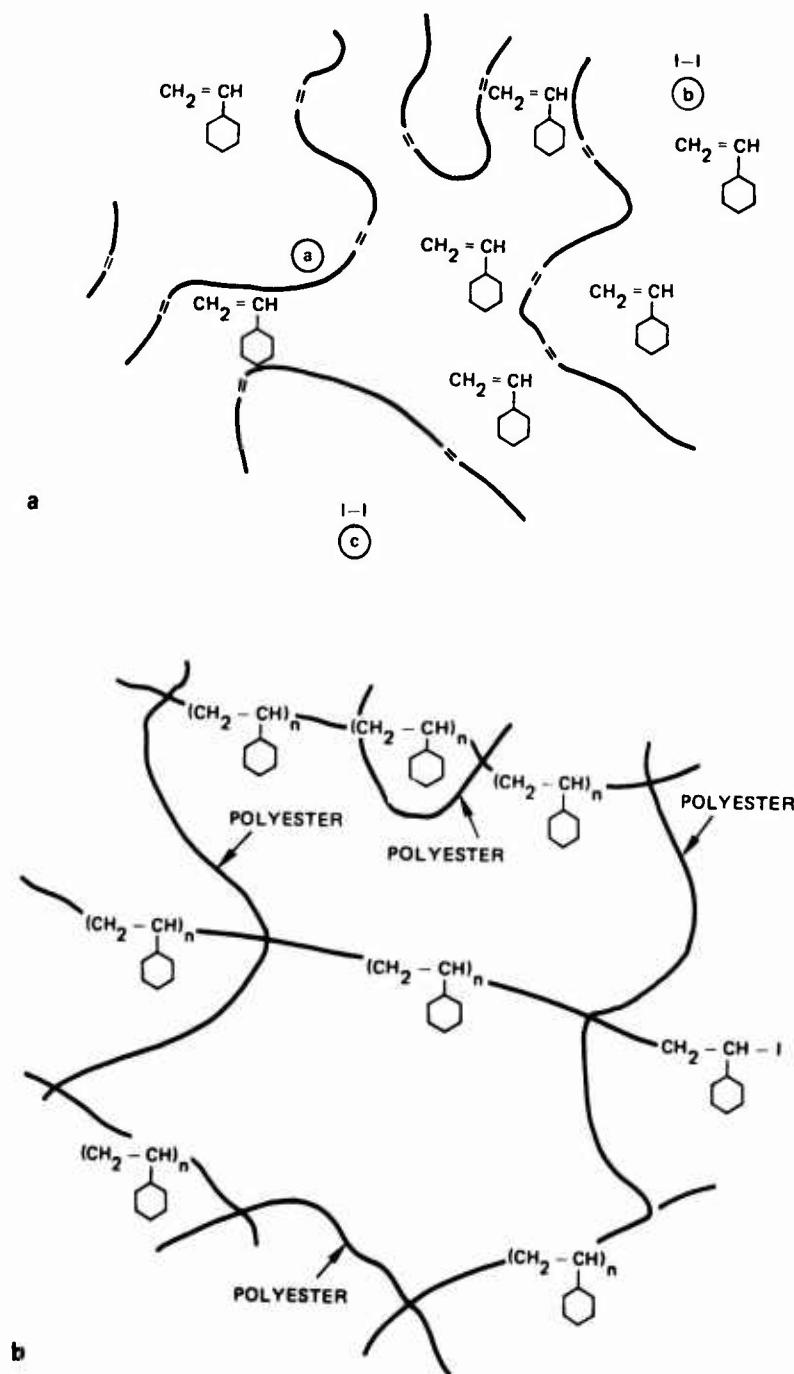


Figure 2

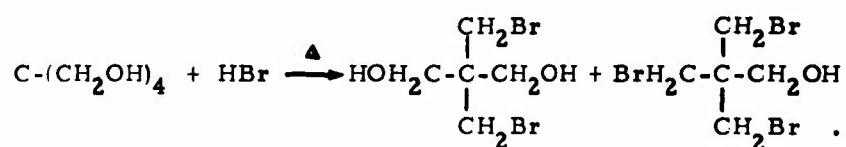
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employed for fire retardance alone. Small amounts of antimony trioxide can markedly inhibit the burning of halogen-containing compositions and are often used whenever opaque products are acceptable or outstanding fire retardance is required.

The most useful fire retarding filler for polyester resins is hydrated alumina. Although the degree of fire retardance obtainable by the sole use of this additive appears to be considerably less than that which can be obtained by the use of a halogenated resin, the relatively low cost of the additive indicates possible utility in combination with more efficient fire-retarding methods. In addition, hydrated alumina assists in reducing the smoke generated by the polyester composition and does not yield corrosive hydrogen halide when subjected to fire conditions. This combination of low cost, low smoke, and reduced corrosivity has led to widespread use of this filler in applications where maximum fire retardance is not required.

Phosphorus compounds and chlorinated waxes have been the most common organic fire retarding additives for polyester resins. Chlorinated biphenyls and organic antimony compounds also have been used to some extent, but the former are now known to pose a health hazard. High-melting insoluble chlorocarbons, such as bi(chloreido)cyclooctane have recently come into use because of their high resistance to leaching, good thermal stability, and good fire retardance efficiency (Pattison and Hindersinn, 1971).

Halogen-containing diols have been suggested as fire retarding monomers for incorporation into unsaturated polyester resins. The only one presently being used commercially, however, is an inexpensive mixture of dibromoneopentyl glycol and tribromoneopentyl alcohol. This product is prepared by the reaction of hydrogen bromide with pentaerythritol at elevated temperatures:



High fire retardant efficiency and good thermal stability of the bromine during thermal processing, its excellent light stability, and ready reaction of the primary alcoholic groups under standard processing conditions give this product all the desirable characteristics of a useful commercial monomer.

Fire retardance can also be incorporated into polyesters by modifying the saturated or unsaturated acid component. Modification of an unsaturated acid has not attained significant commercial importance although chloromaleic acid has been suggested for this purpose. Without the addition of antimony trioxide, such chloromaleic acid resins, however, contain insufficient amounts of chlorine for adequate fire retardance.

Modification of the saturated acid component has been by far the most successful commercial method of preparing fire retarded unsaturated polyester

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resins. Of the commercial fire retarded unsaturated polyesters currently being marketed, the majority incorporate chlorendic acid or its anhydride. Other halogenated dibasic acids used in these polyesters are tetrachlorophthalic and tetrabromophthalic acids. Tetrachlorophthalic acid has not been used appreciably because the fire retardant efficiency of the aromatically bound chlorine is too low to allow the preparation of suitable resins without the addition of auxiliary fire retardants such as antimony oxide. The greater fire retardance of tetrabromophthalic anhydride permits the preparation of unsaturated polyester resins with excellent fire retardance at bromine contents as low as 15 percent by weight.

Another method of incorporating fire retardance into polyester resins involves the addition of suitable halogen- or phosphorus-containing crosslinking agents. Although various degrees of fire retardance can be obtained using this method, the cost of the modified unsaturated compounds generally precludes their use in sufficient quantities to obtain satisfactory fire retardance by this means alone. The crosslinking agents are used to a limited extent in combination with other types of fire retardants to obtain special properties unattainable by other means.

A wide variation in flammability characteristics can be achieved in polyester resins by using one or more of the fire retarding modifications described above. Flame spread ratings of 25 or less, as measured by ASTM E-84, have been attained by using chlorendic acid in conjunction with antimony oxide. These low flame spread ratings can be obtained in the absence of opacifying antimony using the more efficient bromine monomer described above. Recent data indicate that combinations of chlorine and bromine can yield even better fire retardant compositions than can be obtained by using either halogen component alone.

Both fire retarded and conventional unsaturated polyester resin formulations yield copious amounts of smoke when exposed to fire because styrene is the major product of pyrolytic decomposition and styrene burns with a very smoky flame. High smoke values have only been marginally reduced to date by the use of relatively large amounts of inorganic fillers such as aluminum hydrate. Although considerable research is currently being carried out industrially to overcome this disadvantage only minor improvements have been achieved.

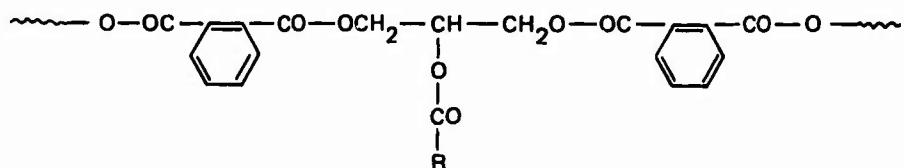
The relative toxicity of halogenated polyester resins has been a subject of considerable discussion ever since their introduction in 1953. Generally, the chlorine contained in these compositions has been shown to be converted largely if not quantitatively, into hydrogen chloride in a fire. Only trace amounts of phosgene have been identified. The relative toxicity of newer bromine-containing resins has not been reported to date. The effect of added quantities of phosphorus or antimony compounds upon the toxicity of pyrolytic gases has not been evaluated.

6.4.3 Alkyd Resins

Alkyd resins are unsaturated polyesters, but differ considerably in their

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structure from styrenated polyesters. The first stage polymer is a condensation product of a dibasic acid (usually phthalic acid) and a dihydric alcohol (typically ethylene glycol). The unsaturated carbon-carbon bonds, however, do not result from copolymerization with an unsaturated dibasic acid or alcohol, but from incorporation of vegetable oils such as linseed oil, soybean oil, or tung oil. These oils are triglycerides containing unsaturated carbon-carbon bonds in the fatty acid components. The oil is usually reacted directly with glycol to form a monoglyceride, which is then reacted with acid to form alkyd resin. Thus, in these resins, the unsaturation occurs not in the main chain of the polyester but in its side chains as illustrated schematically by the formula:



where R is the fatty acid residue. Crosslinking (hardening) to form the second stage resin is accomplished not by copolymerization with styrene but by air oxidation of the unsaturated groups. Oxidation is usually aided by the addition of certain "driers" such as cobalt naphthenate and lead soaps. Properties are modified preponderantly by varying the kinds and amounts of fatty acids. The industry distinguishes long (high oil content) and short (low oil content) alkyds (Vandersall, 1971; Mraz and Silver, 1967).

Alkyds are used almost exclusively as surface coatings, and it has been estimated that in the United States one half of the surface coatings are of this type. Alkyd coatings are of value because of their comparatively low cost, durability, flexibility, gloss retention, and reasonable heat resistance. They may be modified with rosin, phenolic resins, epoxy resins, and monomers such as styrene.

Because of their wide use as coatings, the fire safety characteristics of alkyds are generally modified either by formulating them as intumescent coatings or by incorporating the conventional halogen-antimony oxide fire-retardants. Of these, the two most generally used are the addition of chlorinated waxes as halogen containing additives, or the incorporation of chlorendic acid or some other halogenated carboxylic acid in the polyesters.

Antimony compounds, generally antimony oxide, are added as one of the pigment filler ingredients at the final formulation of the coating. This approach can lead to either an intumescent or a nonintumescent coating. Chlorendic acid based nonintumescent paints have been used fairly extensively by the Navy since 1945.

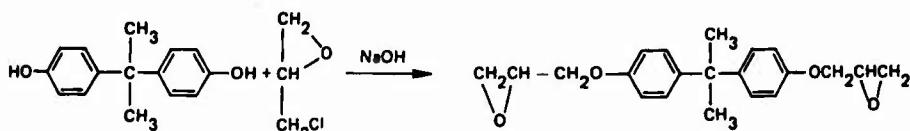
6.4.4 Epoxy Resins

Epoxy resins are specialty thermosetting resins that have developed a signi-

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fificant market as adhesives and coatings, in reinforced laminates, and in molding and casting applications because of a unique combination of properties. The most important of these properties are excellent adhesion, corrosion resistance, toughness, and abrasion resistance. More than 80,000 metric tons were sold in 1974.

Epoxy resins generally are prepared by reacting a first stage polyfunctional epoxy compound or resin with a basic or acidic crosslinker (or "hardener") to yield a thermoset product crosslinked by ether linkages. The basic epoxy resin can be prepared in a variety of ways although the most common is the reaction of a polyphenolic compound with epichlorohydrin. Using bisphenol A as an example, the reaction is schematically illustrated below:

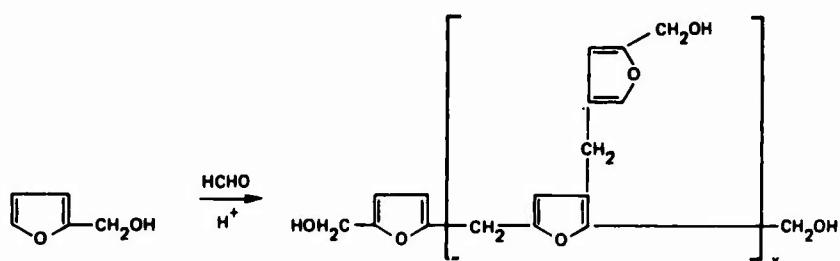


In addition to bisphenol A, a variety of resins also are produced commercially from phenolic novolaks, cycloaliphatic dienes, and other inexpensive intermediates. The prepolymer can be cured with a variety of crosslinking agents (often incorrectly called catalysts) through the epoxy and hydroxyl groups. These hardeners can be based on amines, anhydrides, and Lewis acids. When reactive hardeners such as amines or anhydrides are used, the hardener is chemically incorporated into the cured resin by reaction with epoxide groups. Thus, the properties can be varied considerably depending upon the nature and chemical composition of the curing agent.

Although epoxy resins normally are flammable, their flammability can be reduced considerably by the use of a variety of phosphorus- or halogen-containing additives or reactive monomers (Conley and Quinn, 1975; Lyons, 1970). Tris(2,3-dibromopropyl) phosphate is one of the most common fire retarding additives, and tetrabromobisphenol A is by far the most widely used reactive fire retardant. The need for fire retardance in epoxy resins has been relatively small. Consequently, a relatively small amount of fire retardant epoxy resins is sold annually.

6.4.5 Furan Resins

Furan resins are prepared by reacting furfuryl alcohol and an aldehyde — most frequently formaldehyde-(Siegfried, 1967). Urea often is used as a modifying agent. The chemical reaction in the production of the first stage resin is indicated below:



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The resins are hardened *in situ* with an acidic substance added just before application. A typical curing agent would be p-toluenesulfonic acid.

Furan resins, known for their superior chemical resistance, are used as coatings, adhesives, and reinforced laminates. The volume of resins produced annually is relatively small and has been limited in the past because of the dark color of the resins and limited availability of furfuryl alcohol.

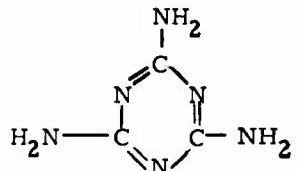
No specific literature reference describes fire retardant methods for furan resins, but fire retardant formulations are available commercially.

6.4.6 Amino Resins

Amino resins are thermoset resins prepared by the reaction of an amino compound with an aldehyde. The two most important commercial materials are based on urea,



and melamine,



Although many different aldehydes have been explored as components for amino resins, formaldehyde is the only one of commercial significance (Widmer, 1965; Sunshine, 1973). In contrast to phenol-formaldehyde resins, amino resins are colorless and generally harder.

In commercial production, the amino compound is reacted with formaldehyde in an aqueous solution under careful control of pH to yield the first stage resin. The reactions are much like those of phenol and formaldehyde. The fusible first stage resin can be compounded with an acidic curing agent and a variety of fillers, reinforcing agents, and colorants, depending upon the application in which it is to be used. This intermediate product, which is the form sold commercially, is then converted into the final thermoset product by application of heat and pressure.

Amino resins find their greatest utility in decorative applications where the hardness can be used to best advantage. Some of their more important applications are dinnerware, decorative laminates for table tops, paper resins, plywood adhesives, and fabric finishes. These wide and varied applications have led to a continually increasing market.

Little work has been done to develop fire retardance in amino resins because

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of their relatively high heat resistance, low flammability, and predominant use in applications where flammability is relatively unimportant. A variety of phosphorus and boron compounds have been used to reduce flammability. Examples of the type of compounds that have been reported as a suitable fire retardant for amino resins are: a mixture of dialkylphosphonate and phosphoric acid, ammonium salts of phosphoric acid, tris(2,3-dibromopropyl) phosphate, and phosphoryl triisocyanate.

Because of their reactivity with a variety of phosphorus compounds and hydroxylic materials like cellulose, mixtures of a phosphorus acid and a urea or melamine resin have found extensive uses as fire retarding finishes for cotton fabrics. A mixture of pyrophosphoric acid and a melamine-formaldehyde resin is the basis for a permanent fire retarding finish.

6.5 Specialty Plastics

This somewhat arbitrary subdivision comprises those materials that are relatively high priced, have certain particularly outstanding properties, and are produced in relatively small volumes for specialty applications. The materials in this group fall into three general categories: (1) aromatic and heteroaromatic polymers that are generally used for their high-temperature capabilities; (2) fluoropolymers that are generally used for their resistance to temperature, chemicals, and combustion; and (3) chlorinated polyethers. Resins discussed in this section may be either thermoplastic or thermosetting.

6.5.1 Aromatic and Heteroaromatic Polymers

Included in this class are aromatic polyimides and poly(imide-amides), poly(aryl ethers), poly(aryl sulfides), poly(aryl sulfones), and aromatic polyesters. A variety of other aromatic and heterocyclic polymers have been investigated intensely over the past decade. These include polyphenylene, polybenzimidazoles, polyquinoxalines, and polyoxadiazoles. Some of these polymers have outstanding thermal and oxidative stabilities and high degrees of fire resistance; however, for various reasons they have not been commercialized. General information on many of the polymers discussed in this section is contained in the book by Lee, Stoffey, and Neville (1967).

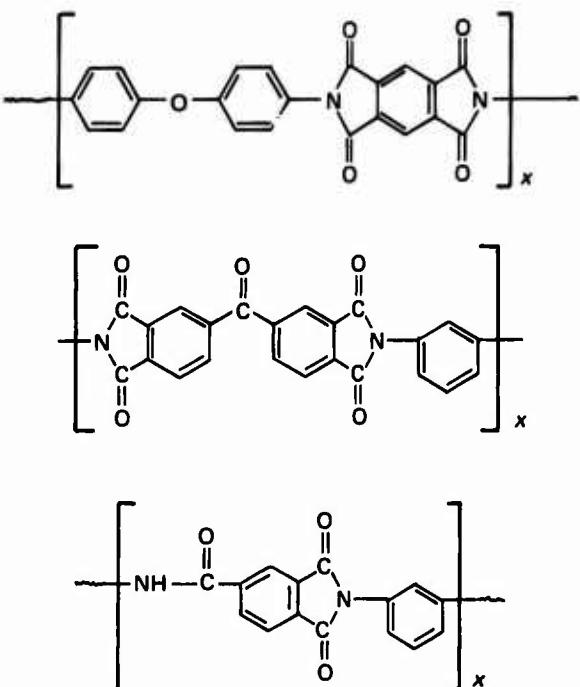
Aromatic and heteroaromatic polymers form char to varying degrees and are the least flammable of any of the polymers that do not contain halogens. The ability to form char not only reduces the available volatile fuel, but also insulates the virgin material beneath the char.

Utilization of the outstanding fire safety characteristics of these polymers is currently hampered by high costs that include cost of the intermediates, cost of making the polymers, and fabrication costs. Each of these elements is generally significantly higher than the corresponding cost for one of the conventional large-volume polymers.

MATERIALS: STATE OF THE ART

6.5.1.1 Polyimides and Poly(imide-amides)

Aromatic polyimides and poly(imide-amides) and their modifications exist in a variety of chemical structures and physical forms. They find applications as injection moldings, compression moldings, laminates, films, foams, and coatings (Hirsch and Kaplan, 1974; Mallet and Darmony, 1974). Their outstanding features are oxidative stability and dimensional stability at elevated temperatures for extended periods of time. Typical polymers are:

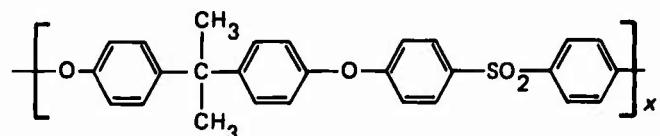
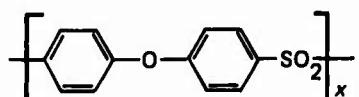
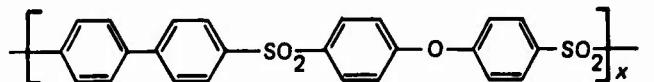


Aromatic polyimides are characterized by high char formation on pyrolysis, low flammability, and low smoke production when immersed in a flame. Primary products of pyrolysis of the first polymer illustrated above are reported to be CO (61 percent), CO₂ (30 percent), H₂O (5 percent), and trace amounts of hydrogen, aniline, phenol, benzene, benzonitrile, hydrocarbons, ammonia and hydrogen cyanide. The char yield was about 60 percent of the initial weight (Bruck, 1974; 1965; 1965a). The oxidative pyrolysis studies on imides and imide-amides have been summarized (Conley and Gaudiana, 1970).

6.5.1.2 Aromatic Polyethersulfones

Among the commercially available polyethersulfones are the following (Leslie, et al., 1974):

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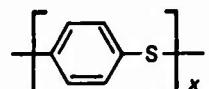


These are strong, tough, rigid engineering thermoplastics with good thermal stability and creep resistance. Thermal endurance, high temperature use limits, cost, and ease of processing vary with structure. Those with higher temperature stability have been more expensive and difficult to fabricate. These materials are finding applications in the electrical, automotive, and aircraft industries where special combinations of mechanical, thermal, and/or fire resistance properties are desired. The polyethersulfones have also been used in blends with other polymers to upgrade their performance.

Aromatic polyethersulfones, along with some newer polyimides and poly(phenylene sulfides), are among the most fire resistant non-halogen-containing thermoplastic polymers. The materials that are most difficult to burn are also the most difficult to process. Their fire retardance is probably due to their char-forming tendencies. Few data are available on products of combustion and their toxicity. Additives, (phosphorus and/or halogen) have been incorporated in some formulations to further improve fire resistance.

6.5.1.3 Poly(phenylene sulfide)

This polymer has the simple structure ,



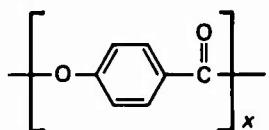
It is a high melting (285°C) crystalline material of outstanding chemical resistance, thermal stability and fire resistance (Bailey, 1974). It is available in grades suitable for coating, injecting molding, and compression molding. It does not have the toughness of polyethersulfones and poly(aryl ethers) and is generally used as a fiber-filled material. Rigidity is retained up to 250°C and the polymer is unaffected by long exposure at 230°C . Major uses are as chemical, and thermal-resistant coatings, as molded parts for pumps, valves, impellers, seals, etc., and as electrical parts.

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Poly(phenylene sulfide) is a char former. In an inert atmosphere essentially no volatiles are evolved below 500°C and 40 percent char remains at 1,000°C. Fire resistance is comparable to that of the best polyethersulfones. It is probably the least flammable of any of the nonhalogen containing thermoplastics. No information is available on the pyrolysis or combustion products.

6.5.1.4 Aromatic Polyesters

An aromatic polyester prepared from p-hydroxybenzoic acid with the structure,



was introduced in 1970 by Carborundum Co. under name of Ekonol®. The polymer is highly crystalline and not completely melted even at its decomposition point (540°C). It has been shown to be thermally stable in air for extended periods at 315°C. Because of its high thermal stability, the polymer can be fabricated by compression sintering at 430°C under pressures of 5,000 psi. Coatings of this polymer on various metals also can be obtained by feeding the polymer powder into a helium gas plasma arc. Because of the difficult fabrication techniques required, its use is limited to such relatively small scale applications as electrical insulators and circuit boards, self-lubricating bearings, and slip free coatings for household cooking utensils and automobile piston rings. The limitation of the polymer to small scale applications and metal coatings does not make its fire resistance especially important commercially (Economy et al., 1970; Economy et al., 1972-1973).

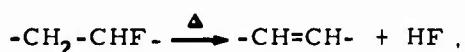
The flammability of this polymer has not been discussed to date.

6.5.2 Fluorocarbon Polymers

The fluorocarbon polymers cover a range of structures from poly(vinyl fluoride), $-CH_2-CHF-$, to polytetrafluoroethylene, $-CF_2-CF_2-$. These materials differ significantly in properties, degradation characteristics, and flammability aspects and will be discussed individually.

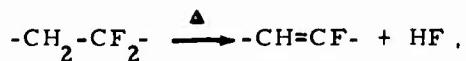
Thermal degradation of all types of fluoropolymers has been reviewed recently by Wright (1970).

There are three areas of potential hazard from toxic products of combustion and/or pyrolysis of fluorocarbon polymers. In polymers that contain both hydrogen and fluorine [poly(vinyl fluoride) and poly(vinylidene fluoride)] the elimination of hydrogen fluoride:

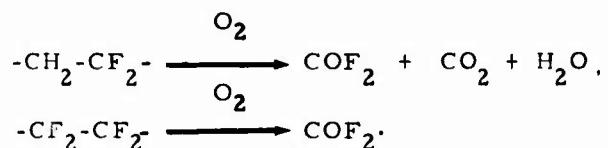


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and



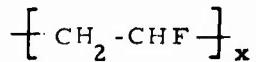
is an obvious danger. For compounds that have two fluorine atoms on a single carbon [poly(vinylidene fluoride) and polytetrafluoroethylene] the potential exists for formation of carbonyl fluoride (fluorophosgene) which readily hydrolyses to HF and CO₂.



There also is a potential for the formation of specific toxic fluoro compounds such as fluoracetic acid and perfluoroisobutylene (Hamilton, 1963). The presence of fillers and additives can change the course of pyrolysis or oxidation of some fluoropolymers to increase the hazard of toxic product formation.

6.5.2.1 Poly(vinyl fluoride)

Poly(vinyl fluoride),



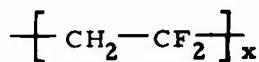
is sold only in film form (Tedlar® film). It is widely accepted for surfacing and also industrial, architectural, and decorative building materials. Its attributes are outstanding weatherability; inertness to solvents, chemicals and stains; as well as excellent abrasion resistance and cleanability (Albisetti, 1973). Current applications include surfacing film for wall panels, vinyl fabrics, aluminum siding, hard board panels for siding, and aircraft and automotive interiors.

Although chemically quite similar to poly(vinyl chloride), poly(vinyl fluoride) is much more flammable. Poly(vinyl fluoride), like PVC, appears to pyrolyze in two stages. There is no weight loss up to 250°C. Hydrogen fluoride begins to evolve at about 250°C. At higher temperature, considerable chain scission occurs with formation of volatiles, which form fuel for the fire. Hydrogen fluoride is much less efficient in quenching gas phase combustion than hydrogen chloride or hydrogen bromide. It is known that pigments and other additives can affect the degradation characteristics of poly(vinyl fluoride) and other fluorinated polymers. Little information is available on how these affect the nature and amount of combustion products (Butler and Erbaugh, 1973).

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6.5.2.2 Poly(vinylidene fluoride)

Poly(vinylidene fluoride),

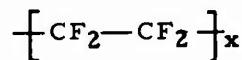


is fabricated by molding, extrusion, and coating. Its outstanding combination of physical, electrical, thermal, and chemical properties account for its major markets in electrical insulation, chemical processing equipment, and long-life finishes for metal siding. It is widely used in the electronics industry and as jacketing on aircraft wires (Michand, 1973).

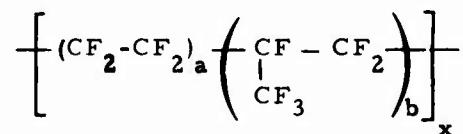
Poly(vinylidene fluoride) is thermally more stable than poly(vinyl fluoride), but not so stable as polytetrafluoroethylene. Rapid pyrolysis occurs at about 425°C with evolution of hydrogen fluoride and formation of a char that amounts to about 40 percent of the initial weight (Wright, 1970). Little information is available on the burning of poly(vinylidene fluoride), or the combustion products formed, apart from hydrogen fluoride. From its structure and mode of pyrolysis it would be expected to be quite flame resistant.

6.5.2.3 Polytetrafluoroethylene and Fluorinated Ethylene-Propylene Copolymer

Polytetrafluoroethylene (TFE),



and fluorinated ethylene-propylene (FEP) copolymer,

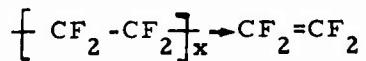


are composed wholly of fluorine and carbon. The major difference in the two polymers is the lower melting and easier processing of FEP. These polymers are dense, chemically inert, thermally stable, and have low coefficients of friction. The applications, based on these properties, are in the chemical, electrical, and mechanical areas. Electrical uses include aircraft and other wiring, and molded insulators. Use in bases, hydraulic systems, valves, seals, linings, and gaskets take advantages of the chemical inertness of these polymers.

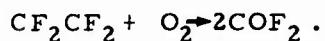
TFE and FEP are certainly among the least flammable of polymers, and their LOI is about 95. They do not support combustion. At about 500°C, TFE pyrolyzes

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almost completely to the fluorolefin monomers,

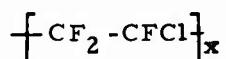


Wright (1970). These monomers can oxidize under certain conditions to carbonyl fluoride a corrosive toxic gas.



6.5.2.4 Chlorotrifluoroethylene (CTFE) Polymers

Chlorotrifluoroethylene polymers,



are similar in many respects to the completely fluorinated materials. They are generally more rigid and expensive, and somewhat less thermally stable than TFE or FEP polymers. Their applications are based on chemical resistance, low water vapor transmission, good electrical and mechanical properties, and processability. Uses include insulation for hook-up wire and cable jacketing, process valves, fittings, seals, tubing film, containers and closures for corrosive materials, and packaging medical supplies.

Various copolymers of CTFE with vinylidene fluoride and with ethylene also are available and show improved processability and other differences. The 1:1 ethylene copolymer is a high-impact material with mechanical properties comparable to nylon 6. It is marketed under the tradename Halar® and is resistant to most corrosive chemicals and organic solvents. Its barrier properties are excellent (Toelcke, 1973). Its applications are generally the same as for CTFE with the addition of uses as specialty fibers, film for aircraft interiors, and cable insulation.

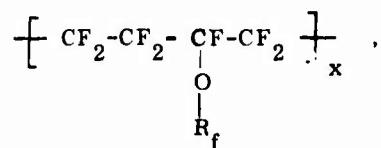
CTFE polymers, just as their completely fluorinated analogs, are very resistant to burning. They undergo pyrolysis at 300 to 350°C (i.e. 100 to 150°C lower than TFE polymers). Pyrolysis produces largely the monomer but also significant amounts of volatile oligomers (low molecular weight polymers). Copolymers that contain vinylidene fluoride or ethylene also can produce hydrogen fluoride and/or hydrogen chloride on pyrolysis.

The 1:1 ethylene copolymer forms a friable char on exposure to flame and does not melt and drip away from the flame. It has a LOI of 60 (Toelcke, 1973).

6.5.2.5 Perfluoroalkoxy Polymers

These polymers have the general formula

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where $\text{R}_f = \text{C}_n\text{F}_{2n-1}$. A new class of completely fluorinated vinyl polymers (fluoro-vinyl ethers) introduced in 1972 resembles the FEP fluorocarbon resins, but have improved high-temperature properties (creep, melting point, and thermal stability). Applications include chemical liners for valves, pumps, and pipes, heat shrinkable tubing and electrical wire insulation, and many types of molding objects. Film and sheet have excellent flex life.

They are comparable in fire resistance to polytetrafluoroethylene (LOI ~ 95) and the products of pyrolysis would be expected to be similar.

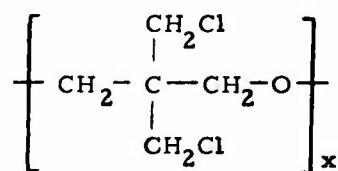
6.5.2.6 Ethylene-Tetrafluoroethylene Copolymer (ETFE)

This material was introduced commercially in 1972 under the tradename Tefzel®. It has many of the properties of the perfluoro polymers, the chlorofluoro polymers and copolymers. These properties include good chemical resistance, electrical properties and weather resistance. Its mechanical, thermal, and abrasive properties also are good and it can be processed by conventional methods. Applications include molded items for gears, pumps, automotive parts, electrical items, and liners. Wire and cable uses cover computers and from hook-up wires to heavy cables. Its service temperature limit is about 150°C.

No data are available on the pyrolysis or combustion of this polymer. Given its structure, hydrogen fluoride would be expected to evolve during pyrolysis, as it does with poly(vinylidene fluoride). Its flammability is similar to that of poly(vinylidene fluoride) and has an LOI of 30.

6.5.3 Chlorinated Polyethers

Poly(2,2-di(chloromethyl) propylene oxide):



is a chlorinated polyether prepared from the monomer by polymerization in inert solvents using Lewis acid catalysts, (Boardman, 1968).

The polymer, a light-colored thermoplastic containing 45.5 percent chlorine by weight was sold commercially under the tradename Penton®. It was a high-

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priced specialty polymer used in relatively small quantities; primarily in applications where its excellent corrosion resistance and dimensional stability are of advantage. Common applications are pipe linings, flow meters, valves, and tank linings.

Penton® resins' flammability is higher than might be expected from the relatively high thermal stability of the halogen in the polymer. This property is indicated by a limiting oxygen LOI of 23.

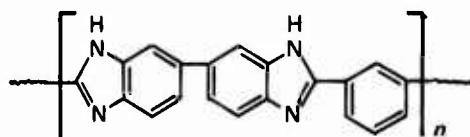
6.6 New Materials Under Development

"Improved" versions of conventional and specialty plastics are continuously being investigated and a limited number are introduced. They are generally different copolymers, new blends, new compositions with different amounts and types of fillers and additives etc. Recently, there has been great activity in such variations to improve fire safety characteristics. No attempt is made to document these changes, but the following summary identifies some of the more fundamentally different new materials that offer potential for improved fire safety. These materials are under various stages of development and study (Lee, Stoffey and Neville, 1967).

6.6.1 Heteroaromatic Polymers

Since 1961 considerable effort has been spent on the synthesis of polymers that retain their properties at high temperatures. The impetus for this work arose from the synthesis of polybenzimidazole by Vogel and Marvel (1961) and the work on polyimides by Sroog, et al., (1964). These materials and the follow-up structures were characterized by being composed primarily of aromatic and heteroaromatic rings. This structure generally leads to high char formation and low flammability.

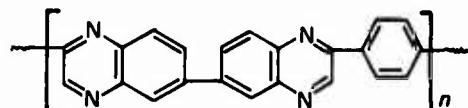
Polybenzimidazole (PBI),



has been extensively studied, particularly for fibers, but also for matrix resins, adhesives, coatings, and foams. It has excellent fire resistance in all physical forms. A major problem with use of PBI for plastic applications is the difficulty in fabrication. This is generally true of all high-char-forming heteroaromatic polymers. They are usually fabricated from a prepolymer, the conversion to final polymer taking place in the mold in much the same way in which thermosetting resins are handled.

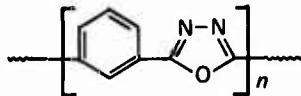
Many other heteroaromatic structures have been studied. Among these are:

polyquinoxalines
(Sorensen, 1961;
Stille and Arnold, 1966),

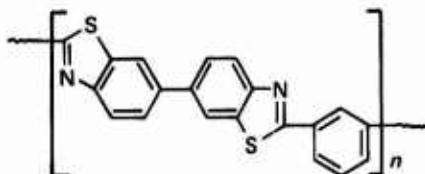


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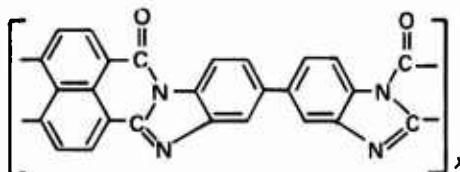
polyoxadiazoles
(Hergenrother, 1970),



polybenzothiazoles
(Hergenrother, 1965),



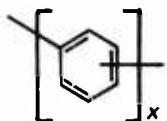
and BBB, pyrrones, and related
"ladder" polymers (Bell et al.,
1967; VanDeusen et al., 1968).



All of these suffer from relatively high cost of raw materials, polymer preparation, and fabrication.

6.6.2 Polyphenylenes

Polyphenylene,



represents another class of high-char-forming resin that has good resistance to burning. Various routes to these materials have been reported (Long, et al., 1966; Ried and Freytag 1968; Kovacic et al., 1964). Cost and/or relatively expensive processing methods have been limitations.

Recently, a new class of thermosetting polyphenylenes, the H-Resins, were announced (Jablonec et al., 1974). These materials are reported to be readily curable and useful as filled, reinforced, or unfilled materials. Their LOI is stated to be greater than 55.

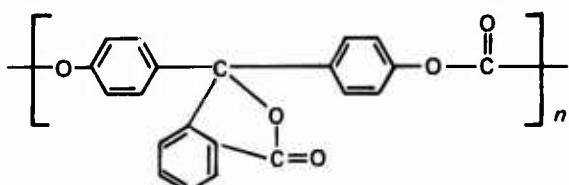
6.6.3 Aromatic Polyesters

A variety of aromatic polyesters with potentially improved fire safety characteristics have been reported in various stages of development. The improvements in the fire safety characteristics of these materials are based on increased char formation.

Morgan (1965, 1970) has synthesized a large number of aromatic polyesters

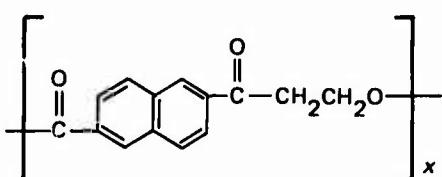
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with large crossplanar and large three-dimensional substituents. Many of these polyesters have high softening points and produce large amounts of char under pyrolysis. One of these, the polycarbonate from phenolphthalein,



has been found to be potentially useful as a fire resistant glazing material for aircraft (Fohlen and Sawko, 1973).

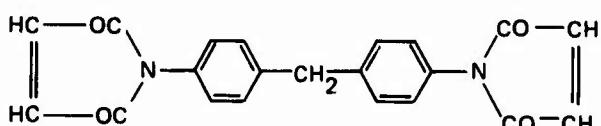
Teijin Ltd. (Japan) has announced developmental quantities of poly(ethylene naphthenate) (PEN) in film form ("Q" film),



which might be expected to have greater resistance to burning than poly(ethylene terephthalate). Unitika Ltd. (Kyoto, Japan) has reported (Sakata 1974) on a polyarylate based on iso- and terephthalate esters of bisphenol A. Its flammability is reported to be less than that of conventional polycarbonates.

6.6.4 Bis-Maleimides

This type of polymer was developed to overcome some of the fabrication deficiencies of the polyimides. The monomer,



is thermally polymerized with evolution of little or no volatiles to give a very thermally resistant, high-char-forming, low flammability product (Mallet and Darmony, 1974). Bis-maleimides have been investigated primarily as matrix resins for composites (Gilwee et al., 1973).

6.7 Composites and Laminates

An enormous quantity of composites and laminates; made from various synthetic plastics, wood products, various fillers, reinforcing agents, and adhesives;

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is produced annually in the United States. Like fiber blends, composites and laminates may pose special fire hazards. In many cases the exact composition of these materials is proprietary. In any case, however, their fire performance cannot be predicted from a knowledge of the performance of the components. The unsaturated polyesters, phenolics, epoxies, and amino resins, are used most often in the manufacture of composites and laminates.

CHAPTER 7

FOAMS

7.1 Introduction

Solid foams occur naturally (e.g., pumice, meerschaum, sponge, and cork). Synthetic foams can be made from practically any polymer. Foamed natural and synthetic polymers pose special fire hazards. Their fire safety aspects are considered in this chapter. Although similar in function and in their response to fire environment, composite low-density honeycomb and truss-core structures are not considered here.

Polymeric foams are generally complex multicomponent systems that may also contain fibers and various fillers. Their surfaces may be modified to produce a denser "skin." Polymeric foams can be divided into rigid and flexible types, a distinction paralleling that of (unfoamed) plastics and elastomers. Foams are either blown or syntactic. In blown foams, the cellular structure is obtained with the aid of a blowing (or foaming) agent that may be either a liquid (which vaporizes during the manufacturing process), a dissolved gas, or a solid which decomposes to give off gas. Alternately, the gas (CO_2 or water vapor) may be formed as part of the polymerization reaction. Syntactic foams are essentially polymers that contain balloons (tiny hollow spheres of another polymer or glass) as filler and necessarily have a closed cell structure. Blown foams may be of the closed cell or open cell forms. In the latter form, the cells are interconnected. Flexible foams generally contain an open cell structure. Rigid foams are usually of a closed cell structure.

Flexible foams find application mainly in cushions, padding, mattresses, and carpet or rug underlays. Minor areas of use are sponges, weather stripping, and packaging for delicate equipment.

Although some rigid foams are used in sandwich constructions for aircraft, furniture and building structures, the major application of rigid foams lies in the field of thermal insulation. Because of their versatility and low cost, the use of synthetic foams as insulating materials is growing rapidly. This growth is aided by the fact that polyurethane can be quickly foamed *in situ*. This procedure is economically attractive. Flexible polyurethane foam can be applied in the form of rolled goods. Thus, a ceiling can be covered easily with a flexible roll of very effective polyurethane foam.

Rigid closed-cell foams are good thermal insulators, where the flexible foams which are open-cell are not good thermal insulators.

The insulating properties of a particular foam are also controlled largely by the nature of the gas that fills its cells. This substance is normally air, which

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replaces any other blowing gas either during or soon after manufacture. When fluorocarbons are used as blowing agents, they diffuse slowly because their thermal conductivity is generally lower than that of air. It appears that an equilibrium is eventually reached when the ratio of air to fluorocarbon in the cells is about 1:1. Fluorocarbon-blown foams, therefore, are very effective insulators.

7.2 Fire Safety Aspects of Foams

The rate of pyrolysis under the impact of a given heat flux, and the heat generated during the subsequent combustion of the volatile pyrolytic gases, are perhaps the most important variables in determining the fire safety characteristics of polymeric solids (Hindersinn and Wagner, 1967). Since polymer compositions burn only on their surface, the amount of surface area available for combustion is important in determining the rate of combustion and, therefore, the intensity of the flame (e.g., a film burns more easily than a thick molded part). The high surface area per unit weight of material being subjected to pyrolytic conditions necessarily increases the flammability of a foam over that of the polymer composition from which it is made. Burning of polymer foams, therefore, differs in several respects from the burning of solid polymers. The most important difference, of course, is the density and the highly insulative properties of the material. Most commercial plastics have densities in the range of 56-75 lb/ft³ (0.9-1.2 g/cm³). Since many foams have densities of about 2 lb/ft³ (0.032 g/cm³), only about 2.5 to 3.5 percent of the total volume of such a foam is composed of solid polymer. Incorporation of such a high volume of gas into the polymeric structure affects the burning characteristics of the material in several ways. First, since a greater surface is exposed to the oxygen of the air, the rate of pyrolysis and burning is increased. Additionally, the high gas content gives foams a low specific heat per unit volume. Their low thermal conductivity tends to concentrate the heat on the surface of the structure rather than dissipating it to underlying material or substrate. The result is a rapid temperature rise and pyrolysis of the surface material when exposed to a flame. This often leads to an extremely rapid flame spread rate. However, other factors may moderate this effect considerably. For example, the small amount of potentially flammable material per unit volume in low-density foams results in a very small amount of total heat being available per unit area for flame propagation.

Thus, if the foam is a thermoplastic (e.g., polystyrene) the heat of a flame rapidly melts the foam adjacent to it and the material may recede so fast from the flame front that there is no ignition. If ignition does occur, these factors may cause the foam to act as an insulator, so that the fire is extinguished when the flaming liquid drops away carrying the flame front with it. A highly crosslinked thermoset foam, on the other hand, behaves in an entirely different manner. Since little or no melting occurs, the surface does not recede from the flame front and the foam is immediately ignited. The flame then spreads if the foam is flammable. However, a fire retarded foam, under the same condition, can pyrolyze rapidly in the vicinity

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of the flame and leave a carbonaceous char on the surface of the material. This highly insulating char protects the remainder of the material from the effects of the flame. In this manner, a relatively flammable solid is converted into less flammable carbon. Since carbon itself is combustible, the continued impingement of a radiant heat flux can generate continued combustion, but the low density of the surface char generally does not produce sufficient heat to sustain burning in the absence of surface heat radiation.

7.3 Rigid Foams

Like plastics in general, rigid foams may be subdivided into thermoplastic and thermosetting foams. Thermoplastic rigid foams can be prepared from most thermoplastics (e.g., polystyrene, ABS resins, polyethylene, polycarbonate, poly(vinyl chloride)) and they generally melt or depolymerize in a fire (i.e., fragment into small, usually volatile molecules). Some thermosetting foams, such as the phenolics, also characterized as semi-rigid crosslinked foams, do not melt or depolymerize, but, for the most part, char in place instead. On the other hand, crosslinked polyurethane foams may depolymerize, melt, and drip like some thermoplastics.

The fire retardant and other flammability properties of foams can be ranked according to criteria established by Parker et al. (1969). These authors have shown that the pyrolytic char yield at 800°C is a convenient parameter for characterizing certain fire safety aspects of specific foams (e.g., their rate of smoke generation and flame spread). Other properties (e.g., reduction in vaporization rate) may also be induced by increased char production.

Rigid foams may be fire retarded in several ways; including the use of fire-retardant additives such as organic phosphate derivatives either in the foam formulation or in a coating applied to the foamed surface (Bagnoli, 1973; Ishizuka et al., 1973; Batorewicz, 1973). Both techniques effectively reduce the burning rate of the foam surface. A more recent practice is the introduction of an inert inorganic filler to control flame spread and flashover.

An alternate method of achieving fire retardation in foams consists of making them from fire retardant polymers. In one approach, halogens such as chlorine or bromine are introduced into the backbone of the basic polymer (Shone, 1973; Stastny et al., 1973; Yamaguchi, et al., 1973; Anon., 1973). Foams generated from bromoepoxy prepolymers and chlorendic anhydride as curing agent are examples. Brominated polyols have been included in urethanes.

Another approach consists in using high-char-yield materials such as the polyisocyanurates, polyimides, polybenzimidazoles, polyquinoxalines, and polyphenylenes. These polymers directly yield fire retardant foams capable of passing current flammability tests without the need for addition of fire suppressant additives.

The application of cement, gypsum board, plaster, or other inorganic surface coatings onto the surface of a rigid foam have become yet another method of controlling their potential fire spread and ease of ignition.

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Rigid polyurethane foam and expanded polystyrene foam are the volume leaders in the thermosetting and thermoplastic class, respectively.

7.3.1 Natural Foams

Among natural foams, cork is the only important material. Cork is the bark of the cork oak (*Quercus tuber*), which attains unusual thickness. It is composed of the walls of dead cells filled with air and is very light (the density being only 0.24 g/cm^3) as well as elastic, tough, and impervious. Technically, it may be classed as a semi-rigid foam.

Cork and corkboard are excellent thermal insulation materials at low and moderate temperatures. They have been used in military and naval applications for many decades. Cork has good thermal ablation characteristics as do most of the charforming foams, but suffers from a propensity to smoulder and produce huge amounts of smoke and toxic gas at relatively low heating rates. Cork is also used in many decorative applications and for low temperature insulation, particularly in warehouses. In cold storage depots, it has now been largely replaced by the more flammable polyurethane foams which are more efficient insulators. Very little work, if any, has been done to improve the flammability characteristics of this naturally occurring foam. Fire retardant treatments applicable to wood also apply to cork in principle.

7.3.2 Rigid Polyurethane Foams

Rigid polyurethane foam and expanded polystyrene foam are the volume leaders in the thermosetting and thermoplastic classes, respectively.

Polyurethanes are the reaction products of a dihydroxylic or polyhydroxylic compound or resin and a diisocyanate or polyisocyanate (Pigott, 1969). Polyurethane foams are prepared by the controlled introduction of a gas phase during the fundamental reaction so that a permanent cellular structure is produced.

Polyurethane foam technology has been reviewed in detail by Backus and Gemeinhardt (1973) and Gmitter, Fabris, and Maxey (1972).

The fundamental reaction between an isocyanate (RNCO) and an alcohol (R'OH) to yield a urethane is:



The reaction is reversible at higher temperatures. Primary aliphatic alcohols give the most stable urethanes. No urethane bond (except N-substituted derivatives not accessible by the NCO-addition reaction) has been found to be stable above 250°C .

Carbon dioxide is produced when an isocyanate reacts with a carboxylic acid or with water. In the first case,



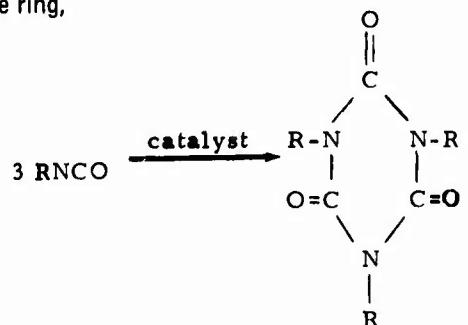
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and the second case,



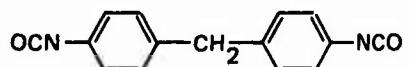
These reactions are often used to supply the gas necessary for foaming.

Another important reaction is the trimerization of an isocyanate to produce an isocyanurate ring,



which introduces a trifunctional crosslink. It is thermally more stable than the urethane and can be used to reduce the flammability of polyurethanes. Isocyanurate structures can be introduced by the use of excess isocyanate in the presence of an isocyanurate catalyst such as a tertiary amine.

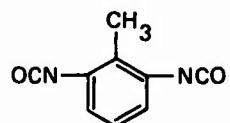
Rigidity of a polyurethane foam is regulated primarily by varying the functionalities of the isocyanate and the polyol as well as the structure of the ester. The most commonly used isocyanates are MDI, TDI, and PAPI. MDI is methylene bis(4-phenylisocyanate),



TDI is tolylene diisocyanate, generally used as 80/20 or 65/35 percent mixtures of the 2,4-isomer,

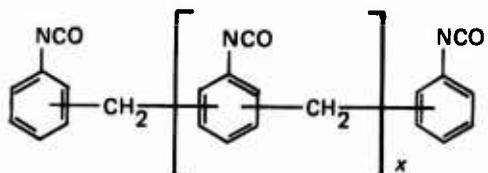


and the 2,6-isomer,



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PAPI has the general formula



Typical polyhydric alcohols are ethylene glycol, glycerol, trimethylol-propane, hexanetriol, pentaerythritol, sucrose, sorbitol, and a variety of polyols (Saunders and Frisch, 1962). Certain naturally occurring materials containing hydroxyl groups, particularly castor oil and its derivatives, also are used.

If the functionality of the reacting components is close to two, essentially linear polyurethanes are obtained. If the functionality of either or both components exceed two, crosslinked structures result. By varying the functionalities and the molecular weight (chain length) of the polyols, varying degrees of rigidity can be obtained. At the same time, other chemical or physical properties also can be varied by the appropriate choice of components. Polyurethane chemistry thus provides rich opportunities for the skill of the formulator.

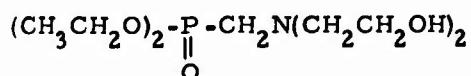
The cellular nature of polyurethane foams generally influences their flammability. A high surface temperature is generated by an ignition source because of low thermal conductivity. This effect can cause almost instantaneous conversion to flammable gases resulting in high surface flame spread and high flaming temperatures once the surface is ignited. Crosslink density significantly affects the flammability of polyurethane foams as noted by Anderson (1966) and others.

The dependence of polyurethane foam flammability upon thermal stability and crosslink density allows the flammability to be reduced considerably by optimization of variables. For example, a respectably rigid fire retardant foam can be prepared in the absence of fire retardant additives by using a highly branched polyol (such as sucrose or a phenol-novolak polyol) in combination with a polymeric isocyanate and/or a suitable catalyst for trimerizing excess isocyanate into thermally stable isocyanurate rings. In this manner, thermally unstable urethane groups are reduced to a minimum while the increased char forming properties of the cyclic polyol structure and the highly aromatic isocyanate or isocyanurate reduce the fuel gas production to a very low level.

In general, fire retardance is imparted to polyurethane foams by the chemical incorporation of halogen and/or phosphorus compounds into the material. Chemical modification of the polyol with phosphorus or a phosphorus-chlorine combination is currently employed in the commercial preparation of fire retardant foams. Halogen alone is generally not satisfactory because the high viscosity of polyols, containing sufficient halogen (typically 25 to 30 percent by weight of chlorine) for effective fire retardance, significantly impairs the processing properties (Hindersinn and Creighton, 1964).

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The use of phosphorus in fire retardant polyurethane foams leads to high char formation combined with easy processing because of the relatively low viscosity of most phosphorus compounds. This combination of desirable properties has made phosphorus compounds, with or without halogen, the most widely used fire retardants in polyurethane technology. Reactive phosphorus compounds, such as Fyrol 6 (Stauffer Chemical Company),



are used extensively. They are added directly to the polyol. Fyrol 6 has enjoyed considerable commercial success and today is perhaps the most widely used fire retardant for polyurethane foams.

Polyurethane foams may be fire retarded also by incorporating nonreactive additives that act as fillers or plasticizers. The most commonly used example of the latter is tris(2,3-dibromopropyl) phosphate. Nonreactive additives have not been used extensively because of their fugitive nature and their tendency to migrate from the foam under many conditions of extended use.

A wide variety of less common methods of preparing fire retardant polyurethane foams have been described in the literature, but will not be discussed here because of their limited commercial utility. Some examples of these atypical methods are:

1. The use of high concentrations of a combination of poly(vinyl chloride) or poly(vinylidene chloride) and potassium fluoroborate (Ricciello et al., 1971).
2. The use of glass beads as fillers (Einhorn, 1965).
3. The use of elementary red phosphorus as a fire retardant additive (Piechota and Wirtz, 1974).

Although polyurethanes themselves are nontoxic, their pyrolysis products have been shown to contain considerable quantities of toxic gases. Significant amounts of hydrogen cyanide have been detected in polyurethane combustion products although the relative toxic hazard of these materials in gaseous mixtures containing large amounts of carbon monoxide has not been definitely established (Sumi and Tsuchiya, 1973).

Petajan, et al., (1975) have recently reported the isolation and identification of a highly toxic phosphate ester in the combustion products of fire retardant urethane foams containing a combination of trimethylolpropane polyol and Fyrol 6 as the active fire retardant. Since even the small concentrations observed were shown to be considerably more toxic to rats than the much larger concentrations of carbon monoxide, the problem of toxicity of fire retarded polyurethane combustion products is now under extensive investigation.

7.3.3 Polystyrene Foams

The use of polystyrene foam for 1974 has been estimated as 189,000 metric

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tons and is expected to increase to 445,000 metric tons by 1980; it accounts for 40 to 50 percent of the total rigid foam market (Houston, 1974). Packaging is the major end use, consuming about two-thirds of the total produced. Construction, appliance, and marine uses make up most of the remainder.

Polystyrene foams can be classified according to density ranges and by processing methods. Expanded bead foams are usually in the density range of 1 to 2 lb/ft³ (0.016 to 0.032 g/cm³) and account for approximately two-thirds of the polystyrene foam used today. The material for bead foaming consists of beads of particles of polystyrene with 6 to 7 percent pentane imbibed into the beads during or after polymerization. These beads are pre-expanded to the desired density of the fabricated product and charged into a vented mold. Steam is injected, the beads expand to fill the interstices and fuse together (Wiman, 1974).

The first commercial polystyrene foam (McIntyre, 1950) was prepared by extruding molten polystyrene, containing methyl chloride as a foaming agent, into large foam logs that were then cut into boards and other shapes. Foamed sheet is prepared by conventional extrusion (Womac, 1974).

The foaming agent (pentane or halocarbon) can be contained in the feed (expandable beads or granules), injected into the molten polymer in the extruder, or incorporated in the feed absorbed on high surface area carriers like silica or clay. Extruded foam sheet and board falls into the 5 to 20 lb/ft³ (0.08 to 0.32 g/cm³) range. Egg cartons as well as meat and produce trays are examples of rapidly increasing usage. Structural foams, with densities of 25 to 50 lb/ft³ (0.4 to 0.8 g/cm³), are formed by injection molding and by expansion casting methods. These materials have a strong continuous skin and a foamed interior. The high-pressure processes give good reproduction of intricate mold surfaces while the low-pressure processes allow use of low cost molds and fabrication of large pieces (Weir, 1969).

Use of structural polystyrene foams is expected to grow rapidly in the furniture, automotive, construction, appliance, and business machine industries. In many cases, these applications involve relatively large parts. The projected consumption of styrenic structural foams has been estimated to reach 180,000 metric tons by 1979 (Martino, 1975).

Polystyrene has a high heat of combustion and burns rapidly with production of dense smoke. Other than carbon monoxide, common to the combustion of all organic materials, there are no known highly toxic combustion products of polystyrene.

Fire retarded versions of foamed polystyrene are more difficult to ignite with small ignition sources, but burn rapidly with high flame spread rates in the high energy environment of an intense fire. The blue-colored fire retarded foam for construction uses is reported to contain acetyl tetrabromide and copper phthalocyanine (Ballast and Griffin, 1965; Ingram and Fogel, 1973). Breakdown products and derivatives of these substances may be expected among the combustion products. Another way to reduce the fire hazard of polystyrene foam involves

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incorporation of a very small amount of additive that promotes molecular weight degradation, softening, and dripping when the foam is heated (Gouinlock et al., 1971). Thus, the foam retracts from the ignition source and/or drips away carrying off heat and flame. Flame spread may be reduced under some conditions; under other conditions such dripping could spread the fire.

In most current uses of foamed polystyrene there is little fire hazard. In packaging applications, the major hazards are in warehousing and storage of large quantities. Hazards in construction, appliance, and marine uses depend greatly on how and where the foam is used. These hazards vary from virtually none, when the material is used as insulation under a concrete slab on the ground, to severe when exposed and unprotected on interiors of building walls. The relative hazards in uses between these extremes, and the effectiveness of additives, chemical modifications, coatings, configuration, coverings, etc., under actual fire situations, need further study and definition.

A major concern is the projected growth and proliferation of structural foams applications. Significantly greater fire hazards may occur as concentrations of such materials increase in living, working, and storage areas.

7.3.4 Polyolefin Foams

Extruded low-density polyolefin foams are made by extrusion-expansion (Miller, 1973). Molten polymer and a foaming agent are blended under pressure and extruded through a die into the atmosphere.

Low-density polyolefin foams, having closed-cell structures, are produced in a two-step method under pressure (Bolduc, 1973). Heating and cooling cycle times are minimized by crosslinking the thermoplastic before foaming. Thin slabs ($\leq 1/4$ in.) can be crosslinked by radiation (Tragesser, 1973). Larger sections are cross-linked by organic peroxides or azo compounds.

The foaming agents are generally either nitrogen release agents (e.g., azobis-formamide or benzenesulfonyl hydrazide) or volatile liquids (hydrocarbons or halocarbons).

Cellular polyolefin (polyethylene, polypropylene) plastics show better thermal, acoustical, and electrical insulating properties than their corresponding solid resins (Bolduc, 1973). They also have better dielectric properties as well as mechanical damping characteristics and are more flexible. Closed cell foams have densities up to 55 lb/ft^3 (0.88 g/cm^3) (Miller, 1973). Open cell foams show high capillarity.

The mechanical strength of a foam is directly proportional to its density (2 to 12 lb/ft^3) (0.032 to 0.190 g/cm^3). Crosslinked polyolefin foams retain dimensional stability above the melting point of the uncrosslinked resin.

Polyolefin foams are used mainly as protective cushion packaging for fragile merchandise. They also find applications in weatherstripping tapes, automotive body joint seal gaskets, backings for wood floorings, and flotation devices. Their dielectric properties make foamed polyolefins of $30\text{--}40 \text{ lb/ft}^3$ ($0.48\text{--}0.64 \text{ g/cm}^3$)

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very useful for telecommunication cable insulation. Crosslinked polyolefin foams can be vacuum formed into items like helmet liners and automotive and aircraft safety padding. Printed polyolefin films, laminated to polyolefin foams, yield decorative and functional composites.

The flammability performance of polyolefin foams is, for the most part, identical with that of the solid plastics. The combustion of polyolefins has been reviewed by Cullis (1974). Flammable blowing agents may increase the fire hazard. When flammability is a concern, the fluorocarbons are the preferred blowing agents (Bolduc, 1973).

Without fire retardant modifications, polyolefin foams burn cleanly at rates of 3 to 6 in./min in horizontal configurations. They have flame spread ratings (ASTM Test E84) of 10 to 20, depending on thickness (Tragesser, 1973).

Cushion packaging and gasket applications rarely, if ever, require fire retardation. Flotation devices (e.g., for aircraft seat cushions), invariably require fire retarding modifications.

Antimony oxide/chlorowax combinations or other aliphatic chlorine sources are generally used to fire retard polyolefin foams (Schwartz, 1973; Howarth, 1973). Because of the higher processing temperature required (up to 280°C) when using azo blowing agents, the antimony oxide/chlorine system is inadequate and, in that case, phosphorus-containing fire retardant systems are preferred (Kuhn 1975).

7.3.5 Poly(vinyl chloride) Foams

The largest use for foam based on poly(vinyl chloride) is in coated fabrics, where the foam is sandwiched between a supporting fabric and a wear surface (Werner, 1972). This arrangement serves as an upholstery material used widely in transportation, and in home, business, and entertainment areas. It is also used as clothes linings and in accessories such as handbags, shoes, and boots.

Chemically blown film has also been used extensively in flooring. A foam lamina can be topcoated with a wear surface and placed onto a solid flooring substrate. It also can be used as a base layer for floors when covered with glass mesh and vinyl chips.

Mechanically frothed plastisol foam has been used primarily for carpet or rug backings and for synthetic turf.

Pressure molded vinyl foam has a relatively small market and is used for life rings and jackets, boat bumpers, athletic paddings and mats.

Rigid foams are being used as laminates with metal and reinforced plastics for applications in construction and aircraft. Moldings and coverings of rigid vinyl foams are also finding extensive acceptance.

Formulations can be quite complex. In addition to the poly(vinyl chloride) homopolymer or copolymer, foams may contain plasticizers such as: dioctyl phthalate, aromatic phosphates, or polymeric plasticizers. They may contain stabilizers, which can be various combinations of Ba, Cd, Zn, or Sn compounds with a

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heat stabilizer, as well as pigments, fillers, lubricants, and chemical blowing agents.

Poly(vinyl chloride) is inherently fire retarded because of its high chlorine content. Flexible PVC foams present increased fire hazards because of the plasticizers they contain. Phosphate ester plasticizers should improve performance as to ignition and flame spread when compared to the more usual phthalate plasticizers.

7.3.6 Phenolic Foams

Phenolic foams are made from one of the oldest synthetic polymers. They are prepared by the condensation of phenol and formaldehyde. Although there has been considerable activity in the area of phenolic foams, these materials have not attained the prominence of the polyurethane foams because of their brittleness and open-celled structure. They have been used for thermal insulation, in the floral market (particularly in Europe), in acoustical panels, in nuclear packaging, and as precursors of carbonized structures.

As previously indicated, there are two general types of first-stage phenolic resins: resoles and novolaks. In general, the novolaks are not as important as the resole resins as foam precursors.

Strong acids are used to cure the resins producing an exothermic reaction with the concomitant formation of water and a foamed structure. Volatile liquids and solid blowing agents are used to produce a more uniform foam since water blowing can cause coarse and nonuniform cellular structures. Poly-halogenated fluorocarbons are preferred (D'Alessandro, 1968). Hydrocarbon and aliphatic ethers also have been used (Compagnie de Saint-Gobain, 1967). Foams with densities of 0.2 to 3.0 lb/ft³ (0.0032 to 0.048 g/cm³) are produced.

The rigid and brittle nature of phenolic foams has been improved by the use of modifiers in conjunction with phenolic resins. Examples of such modifiers are poly(vinyl alcohol), poly(vinyl acetate), and polyamides (Frisch and Saunders, 1973).

Cured phenolic resins have good thermal stability and high tendency to char in an intense fire. Even after the removal of the ignition source, the foams often smolder and char until they are almost completely consumed. This latter phenomenon, called punking, is claimed to be overcome by the addition of boric acid/oxalic acid and ferric/aluminum chloride as the foaming catalysts (Quarles and Baumann, 1967). The addition of antimony compounds is also reported to decrease punking. Chlorinated aromatic compounds are claimed to achieve similar results when included in a phenolic foam formulation.

7.3.7 Urea/Formaldehyde Foams

Urea/formaldehyde (UF) foams were first developed in 1933 (I.G. Farben-industries, 1933). Their low cost and low density in combination with other properties have led to their use in many different applications. In Europe and England, UF

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foams have been used extensively as insulation. Insulation for piping, as well as uses in shipping and displaying of cut flowers, are noted (Frisch and Saunders, 1973).

The UF resins are suitable for foam production in a mole ratio of 1:1.6 to 1.2. Foams are produced by several techniques including the use of hydrocarbons or fluorocarbons, *in situ* generation of carbon dioxide, and dispersion of air into the resin before acid curing of the foam. Foams produced by the hydrocarbon/fluorocarbon routes are generally closed-cell foams, whereas other techniques provide open-cell structures.

Many techniques have been used to decrease friability and improve dimensional stability. A large number of polymers and copolymers have been added before foaming in an effort to improve the mechanical properties of UF foams.

Whereas UF foams can be rated as materials which burn with difficulty, blending of UF with another polymer can decrease the resistance of the foam to burning. Fire retardants, including phosphorus and boron compounds, have been added to decrease the flammability. UF foaming resins have been used in intumescent coatings for the protection of various substrates including wood.

7.3.8 Polyisocyanurate Foams

Isocyanurate-based foams have significantly increased in use during the past decade due primarily to the introduction of low-density foams and the mass production of skin-molded polyisocyanurates (Raymore and Carleton, 1974). The foams are prepared by trimerizing the appropriate isocyanates in the presence of suitable catalysts. They have significantly increased thermal stability when compared to polyurethanes.

The foam can be processed on conventional urethane foam forming equipment. It can also be sprayed and poured in place. Its recommended use temperature is about 140°C. Major applications for the low-density foams are in construction, refrigeration, transportation, and industrial storage tanks.

Integral skin foams represent a new opportunity for polyisocyanurate foams in the furniture industry as replacement for polyurethane foams. Their use temperature is about 50°C higher than that of the polyurethanes and their improved flame resistance, low fuel contribution, and low smoke generation make them attractive for applications where flammability is a serious consideration.

7.3.9 Foams From Thermally Stable Synthetic Polymers

In recent years a large number of aromatic and heteroaromatic thermally stable polymers have been synthesized, but relatively few have become commercial (Hirsch and Kaplan, 1974; Mallet and Darmony, 1974). Relatively high priced, they have been used only in small volume to date. Foams made from two of these classes of polymers (i.e., the polyimides and polybenzimidazoles) are reviewed here as follows:

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7.3.9.1 Polyimide Foams

Aromatic polyimides demonstrate outstanding thermal stability, low flammability, and high char formation. They have been used in a variety of forms such as films, laminates, compression moldings, coatings, and foams. These polymers have been converted into foams by the liberation of either water or carbon dioxide. Dianhydrides are reacted with amines or isocyanates to form a prepolymer which, when heated, liberates these blowing agents in the final foaming stage. Crosslinked foams have been produced by adding polyols that react with isocyanates to form some urethane linkages.

7.3.9.2 Polybenzimidazole Foams

As is the case with polyimide foams, the prepolymers are prepared and foaming occurs during the last stages of polymerization by the liberation of volatile products (i.e., phenol and water). Crosslinking can be achieved by using polyfunctional reagents or by thermal aging. The foams exhibit excellent resistance to ignition. They form large amounts of char under appropriate conditions.

7.4 Flexible Foams

Flexible foams can be made from practically any elastomer. They are used in a variety of applications, the most important being mattresses, seat cushioning, rug underlay, and carpet backsizing.

When a chemical blowing agent is used in a dry-compounding recipe, the resulting foam rubber is generally referred to as sponge rubber. Sponge rubber is made mostly from natural and from styrenebutadiene rubber, although silicone and fluorocarbon (Viton) sponge rubbers are also available.

Foam rubber latex is made by beating air into compounded rubber latex followed by curing. Fluorocarbons may be added as foaming agents in some processes. A gelling agent, such as sodium silicofluoride or ammonium acetate, may or may not be used to derive what is here called latex foam (Morton, 1973). Natural or styrene butadiene rubber, or blends of the two, are widely used. Polychloroprene (neoprene) latex foam may be used to decrease the fire hazard of mattresses, particularly in naval vessels.

The fire retardation of latex foam has been discussed by Hecker (1968) and that of sponge rubber and latex foam by Fabris and Somer (1973). Approaches used for fire retardation generally are the same as those used with the nonfoamed elastomer except that post-treatments similar, in principle, to those discussed in connection with wood and wood products are possible because of the cellular nature of foams. Thus rubber sponge has been impregnated with slurries of gypsum and cement (Kurz et al., 1964). Polychloroprene foams can be made highly fire retardant by post-treatment with mixtures containing ammonium sulfamate (Carl, 1962) or melamine-aldehyde condensation products (Weissert, 1959). Amounts of

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10 to 35 percent usually are required; no further improvement in fire retardance is noted beyond 35 percent.

Little is known about the smoke and toxicity aspects of sponge rubber or latex foams. According to Gmitter and Maxey (1969), flexible slab polyurethane foam accounts for about two-thirds of all flexible foam. The method for preparing flexible polyurethane foam is not essentially different from that for rigid polyurethane foam. Flexibility is achieved by appropriately varying the structure, molecular weight, and functionality of the polyols used in the preparation. Most flexible polyurethane foams today are made from polyethers.

Methods for fire retarding flexible polyurethane foams are essentially the same as those used with rigid polyurethane foams. Flexible foams, however, burn readily even when fire retarded; a totally satisfactory solution to the pressing problem of fire retardant flexible foam for cushioning has not yet been developed. The novel polymers possessing inherently improved fire safety characteristics, are all made from molecules which are too rigid to yield flexible foams. The phosphonitrilic elastomers are promising and should be evaluated.

CHAPTER 8

FIRE RETARDANT COATINGS

8.1 Introduction

The use of fire retardant coatings is one of the oldest methods for protecting flammable substrates from reaching ignition temperatures and for preventing non-flammable substrates from reaching softening temperatures.

8.2 Nonintumescent Coatings

Although nonintumescent coatings do not provide the same degree of fire protection to the substrate as do intumescent coatings, they should not enhance the spread of flame by rapid combustion or contribute a significant amount of fuel to a fire. They are useful in marine applications, which constitute one of the largest areas for usage of such fire retardant coatings, because ships receive repeated paintings in an effort to provide corrosion protection. As layers of conventional paints build up, they pose a fire hazard regardless of the nature of the substrate (i.e. in the event of fire, the paint may ignite, melt, drip, and cause severe injury and increased damage to the vessel). To prevent this hazard fire retardant coatings were formulated not to sustain combustion, even when thick films were exposed to fire.

8.2.1 Alkyd Coatings

The most widely used nonintumescent fire retardant coatings are based on chlorinated alkyds. A common method for preparing fire retardant alkyd coatings is to use reactive chlorinated diacids or anhydrides such as: chlorendic anhydride or tetrachlorophthalic anhydride. These materials are reacted into the coating compositions using standard alkyd preparation methods, but temperatures in excess of 200°C must be avoided during preparation or dark colored products may result. A typical fire retardant alkyd resin may be prepared from the following ingredients:

	Moles
Chlorendic anhydride	0.740
Glycerine	0.835
Soybean fatty acid	0.917

(Cleaver, 1973). By using the proper chlorinated acids, coatings can be made that have properties comparable to those of conventional coatings in addition to being fire retardant. It is this high performance at relatively low cost that has made chlorinated alkyd coatings so successful.

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The addition of fire retardant additives to alkyd resins also is commonly employed to increase the fire retardance of alkyd coatings. Their use in coatings has been recently reviewed by Lyons (1970), Thiery (1970), and Bhatnagar (1972). Not all fire retardant additives, however, are suitable for inclusion in alkyd formulations because many are not compatible with the paint vehicle or substantially impair the physical properties of the coatings.

Halogenated additives, such as chlorinated paraffins, have been used extensively in fire retardant coatings because of their low cost and their minimal effect on regular properties when used in combination with metal oxides (antimony oxide is the most commonly used metal oxide). The chlorinated paraffins by themselves do not greatly improve fire retardance. The difference in performance contributed by the metal oxide can be illustrated by considering that a chlorine content of over 40 percent is needed to make an alkyd film self-extinguishing (LOI = 21), whereas only 20 percent of chlorine is needed if 7 percent of antimony oxide is present (Birkenhead, 1969; Touval, 1972). Other metal salts are capable of synergism with halogen. Lower cost materials, such as stannic oxide and zinc borate, have recently been used to partially replace antimony oxide with no loss in fire retardance (Bower et al., 1972); however, total replacement probably will detract from performance.

Inert mineral fillers also reduce the flammability of coatings. They act simply by diluting the fire load presented by the combustible organic material; relatively high filler loadings must be used before any significant improvement is seen. This approach is essentially limited to opaque low-gloss coatings. Some fillers, however, do have more than a dilution effect in reducing flammability. Alumina hydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is dehydrated in a fire through a highly endothermic reaction that lowers the oxidation rate (Connolly, 1965). In addition, water vapor is given off which dilutes the flammable gases. When the temperature is lowered sufficiently below the ignition temperature, combustion is retarded. The main disadvantage of high filler loadings is the detrimental effect on abrasion and humidity resistance resulting from high porosity of the paint film.

8.2.2 Miscellaneous Coatings

Other polymers have been used to a much lesser extent in nonintumescent coatings; however, such coatings based upon urethanes (Saunders and Frisch, 1962) and epoxy resins (Lyons, 1970 and Anon., 1971) have been described. Fire retardant heat-cured coatings, based upon melamine formaldehyde and phenol formaldehyde resins may find significant utility on factory coated wood paneling in the future.

Water-based nonintumescent fire retardant coatings, i.e., coatings in which the majority of the diluent is water, have not been developed to any significant degree. The only coatings showing potential in this area are based upon emulsions of copolymers of vinyl chloride with other monomers.

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8.3 Conventional Intumescence Coatings

Intumescence is defined as "an enlarging, swelling or bubbling up (as under the action of heat)" (Webster's Third New International Dictionary, 1961). Intumescence is well demonstrated by the high school chemistry experiment in which sugar is reacted with sulfuric acid. The acid dehydrates the sugar to a carbonaceous char, which is expanded into a foam by the steam produced by the heat of the reaction.

Intumescence coatings have been available commercially for over 20 years. They are used to prevent flammable substrates, such as wood and plastics, from reaching ignition temperatures as well as nonflammable substrates, such as metals, from reaching softening or melting temperatures. A review of intumescence coatings was recently published by Vandersall (1971). The principles of intumescence coating technology are reviewed here, however, in an attempt to relate this technology to that of fire retardant compositions.

8.3.1 Theory

Conventional intumescence coatings contain several ingredients that are necessary to bring about intumescence action. An intumescence catalyst is used to trigger the first of several chemical reactions that occur in the coating film. The coating contains a carbonific compound that reacts with the intumescence catalyst to form a carbon residue, and a spumific compound that decomposes to produce large quantities of gas. The latter cause the carbonaceous char to foam into a protective layer. A resin binder forms a skin over the foam and prevents the escape of the trapped gases. Apart from these key ingredients, intumescence coatings also include many others (e.g. pigments, driers, leveling agents, and thinners) used in conventional coatings. In appearance, intumescence coatings are similar to nonconventional coatings. Unfortunately, most intumescents have one or more of the following drawbacks: poor aging, poor weathering, poor humidity resistance, poor color, poor flexibility, and high cost.

8.3.1.1 The Resin Binder

Virtually every resin binder has been used in the preparation of intumescence coatings. An important requirement of the binder is that it must not harden or crosslink with age since this would have a detrimental effect on its intumescence ability. This precludes the use of many air-drying resins (e.g., alkyds). Thermoplastic resins, such as vinyl polymers and styrene-butadiene polymers, are preferred because they soften or melt at reasonably low temperatures. Another important requirement is that the resin binder must not depolymerize or decompose into flammable volatile fragments.

Chlorinated resin binders, such as chlorinated rubber and vinyl polymers, are especially desirable because they also exhibit a spumific effect by the evolution of

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hydrogen chloride at elevated temperatures while simultaneously contributing significantly to char formation.

8.3.1.2 The Intumescent Catalyst

The main function of an intumescent catalyst is the dehydration of the carbonific compound to a carbonaceous char. Since the addition of an acid compound can impair the coating through the formation of gel, etc., a thermally unstable nonmetallic salt of the acid generally is used. Thus, the acidic catalyst is generated *in situ* when the appropriate temperature is reached under fire conditions. Three inorganic acids — sulfuric, boric, and phosphoric — have been used; the latter being most common. The effect of phosphorus compounds on the fire retardance of cellulosics is well documented (Little, 1974).

Among the inorganic salts, monoammonium phosphate and ammonium polyphosphate are most often employed. Ammonium phosphate has the disadvantage, not shared by ammonium polyphosphate, that it is highly soluble in water. Upon heating, the salt decomposes to ammonia gas and acid. The latter reacts with the carbonific compound to give water and carbonaceous char and is then regenerated.

Organic salts of inorganic acids, such as melamine phosphate and urea phosphate, are also used. Heating produces phosphoric acid and an organic fragment that contributes to the carbonaceous char.

One of the important requirements of an intumescent catalyst is that it must decompose at a lower temperature than the decomposition temperature of the carbonific compound.

8.3.1.3 The Carbonific Compound

The carbonific compound is a polyhydric organic compound, which forms a carbonaceous char when it reacts with the acid produced by decomposition of the intumescent catalyst. It is this carbonaceous char that prevents or retards the flame spread. The carbonific compound can be either monomeric or polymeric. Monomeric carbonifics include sugars, polyhydroxylic compounds of pentaerythritol family and other compounds. Among the polymeric carbonifics are urea/formaldehyde resins, phenolics, pentaerythritol polyurethanes, and starch. An effective carbonific must not only contain a high percentage of carbon to give a strong carbonaceous char, but also have a high hydroxyl content.

Phosphoric acid reacts with the carbonific compound to produce carbonaceous residue by dehydration. Recently, Ellard (1973) has shown that carbonaceous char obtained from many such systems consists predominantly of polyphosphoric acid and phosphate glasses.

8.3.1.4 The Spumific Compound

Spumific compounds decompose when heated, evolving large quantities of nonflammable gases such as ammonia, hydrogen chloride, and carbon dioxide. The

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remaining residue contributes to the carbonaceous char. Commonly used spumifics are melamine, dicyandiamide, guanidine, urea, and chlorinated polymers. More than one spumific may be used so that gas is evolved over a broader temperature range.

The decomposition temperature of a spumific must correspond to the temperature at which the carbonaceous char is forming while still in a molten state. If the gas is released too early, there will be no intumescence. If the gas is released too late, either no intumescence will occur or the char will be very fragile and will not protect the substrate.

8.3.2 Mechanism

For intumescence to occur with the above ingredients, five important and interrelated steps must occur in precise order as follows:

1. The intumescent catalyst decomposes to form phosphoric acid.
2. The phosphoric acid reacts with the carbonific compound to give a phosphate ester.
3. The phosphate ester decomposes to phosphoric acid, water, and a carbonaceous char.
4. The resin binder softens or melts, covering the carbonaceous char and trapping the released gases.
5. The spumific compounds decompose, releasing non-flammable gases that blow the carbonaceous char into the insulative foam protecting the substrate.

Three phases are present when a cellulosic substrate burns. The gas phase consists of flammable gases such as methane and nonflammable components such as carbon dioxide and water. The liquid or condensed phase, which consists mainly of highly volatile tars and organic compounds, is responsible for the flame spread of an organic coating. The solid phase consists of the carbonaceous char that oxidizes slowly and contributes very little to the flame spread. An intumescent coating prevents or slows the flame spread by keeping the flame away from the condensed phase.

8.3.3 Recent Developments

The mechanism just described is quite complicated and, as noted, must be synchronized for best results. Roth and Green (1973, 1974) have recently shown that, by matching the thermal properties of both binder and intumescent agent, synchronization and good fire retardance can be obtained.

They studied a nonconventional system in which a single compound, a substituted benzene sulfonamide, acts as intumescent agent, carbonific and spumific. The preferred intumescent agent appears to be p,p'-oxybis(benzene sulfonamide). Differential scanning calorimetry showed the intumescent agent to possess an exotherm between 275 and 340°C and an endotherm between 340 and 390°C. Therefore, the proper resin binder for this intumescent agent would show thermal

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activity (softening melting, etc.) at a temperature lower than the decomposition temperature for the intumescent agent.

Differential scanning calorimetry showed that a vinyl chloride-vinylidene chloride copolymer binder decomposes between 260 and 290°C, the preferred temperature range. A coating, using this intumescent binder and the above preferred intumescent agent, had a flame spread of 14 (measured with the Monsanto 2 foot tunnel) and a foam height of 14 millimeters. By comparison, a styrenated acrylate binder was found to have thermal activity at between 375 and 430°C, much higher than the decomposition temperature of the intumescent agent. As predicted, this coating system had no intumescent properties; a flame spread of 103 was obtained.

Viscosity of the resin binder at its melting or softening point is of prime importance for good intumescence. If the viscosity were too low, the resin would drip and the intumescent foam would be weak and easily carried away by the air currents produced by the flame. The condensed or liquid phase would then be unprotected and the flame would spread rapidly. If the viscosity were too high, the gases would not be able to expand the char into the protective foam and the coating would behave as a normal nonintumescent coating affording little protection to the substrate.

Another recent development, as reported by Fohler et al. (1970) and by Sawko et al. (1972), is an intumescent coating system using a polysulfide epoxy resin binder. The intumescent agent is the ammonium salt of 4-nitroanilinesulfonic acid, which behaves both as a spumific and a carbonific. It decomposes at 300°C to give ammonia and sulfur dioxide gas. The corresponding weight loss is approximately 50 percent. The nonvolatile residue is believed to consist of polyquinoxalines and polyphenoxazines. Upon further heating, this residue gives a carbonaceous char. Tris(dimethylaminomethyl)phenol is used to crosslink the resin binder. A mixture of equal parts of polysulfide resin and epoxy resin gave the best intumescent properties. When the resin binder consisted of 100 percent polysulfide resin, however, the intumescent layer melted and flowed excessively; when the resin binder consisted of 100 percent epoxy resin, very little intumescence was observed, presumably because of excessive crosslinking. This coating was designed specially for the protection of steel and aluminum substrates and has been used to prevent naval armaments from reaching detonation temperatures.

There is recent interest in the protection of flammable plastic substrates by the use of intumescent coatings. Slysh (1974) reported on the fire retardance of several plastics, including nylon and diallyl phthalate, using a conventional intumescent coating consisting of a vinyltoluene-butadiene resin binder, an ammonium polyphosphate intumescent catalyst, plus dipentaerythritol carbonific compound, together with melamine and chlorinated paraffin spumific compounds. When a 5-mil-thick dry film of this intumescent coating was applied to a glass reinforced

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nylon substrate, the flame spread, as measured on the 2-foot Monsanto tunnel, decreased from a rating of 140 for the uncoated control to 36. The protection afforded by the intumescent foam also can be measured by the insulative values of the control and coated nylon substrate. The insulative value is measured by the temperature increase on the back side of the panel. The lower the increase, the greater the insulative value. An uncoated glass-filled nylon sample had a back side temperature more than 400°C higher than a similar panel coated with a 5-mil-thick dry film. This effect illustrates the thermal protection afforded to the substrate by the intumescent foam.

8.4 Nonconventional Intumescence Coatings

By definition, nonconventional intumescence coatings are those in which the elements of intumescence are built into the binder itself.

8.4.1 Triphenyl Phosphite Modified Epoxy Coatings

A novel clear intumescence epoxy coating has been prepared by the reaction of triphenyl phosphite with an epoxy resin prepared from epichlorohydrin and bisphenol A (Blair et al., 1972). The coating, consisting of 100 percent solids, was prepared by adding the amine catalyst to a premixed epoxy-(triphenyl phosphite) resin just before it was applied. It is proposed that triphenyl phosphite transesterifies a hydroxyl group in the epoxy resin (Barnstorff et al., 1959). The epoxy becomes crosslinked not only by the polyamine curing agent, but also by the phosphite.

The phosphite is chemically bound into the resin; immersion of the coating in distilled water at 50°C for 24 hours did not affect its fire retardant properties. A flame spread of 37, as measured by a modified ASTM E84 test, was obtained with this resin when applied as a 7.6-mil-thick dry film.

Important variables in this coating are the amount and type of curing agent. Maximum fire retardance is obtained with the stoichiometric amount of a polyamine curing agent.

8.4.2 Clear Polyurethane Intumescence Coating

A novel fire retardant clear intumescence coating was reported by Clark et al. (1967, 1968). They used a moisture curing polyurethane prepared from pentachlorophenoxy glycerol ether, triethylene glycol and toluene diisocyanate in a solvent.

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